THE USE OF

7-BENZYLIDENEACENAPHTHENE-8-ONE

IN THE SYNTHESIS OF AROMATIC HYDROCARBONS

by

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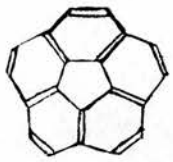
CONTENTS

INTRODUCTION

Part of the work on aromatic hydrocarbons at Edinburgh University is concerned with attempts to synthesise the hypothetical coronindene (I) and its precursors.

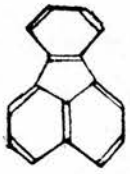


I

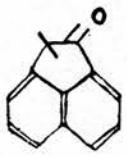
Apart from the practical interest of this highly compact and symmetrical molecule, it has considerable theoretical importance in extending our knowledge of the properties of five membered rings, and the effects of strain on the lengths and directions of bonds in aromatic compounds.

The aim of the work of this Thesis was to prepare and study compounds such as derivatives of fluoranthene (II) which might be precursors of coronindene (I) or its congeners, and the approach adopted was to synthesise suitable fluoranthene intermediates whence these might be obtained. Of the many starting materials available for the preparation of fluoranthenes, acenaphthene-8-one (III) was chosen. Acenaphthene-8-one (III) had been studied by Gow[1], Foggo[2], and Henderson[3] in Edinburgh, but the synthetic advantages of the

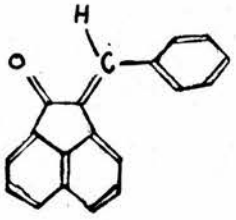
activity of the $-CH_2-CO-$ grouping in this compound were found to be outweighed by the tendency of the molecule to yield a dimer XV by self-condensation.



II



III



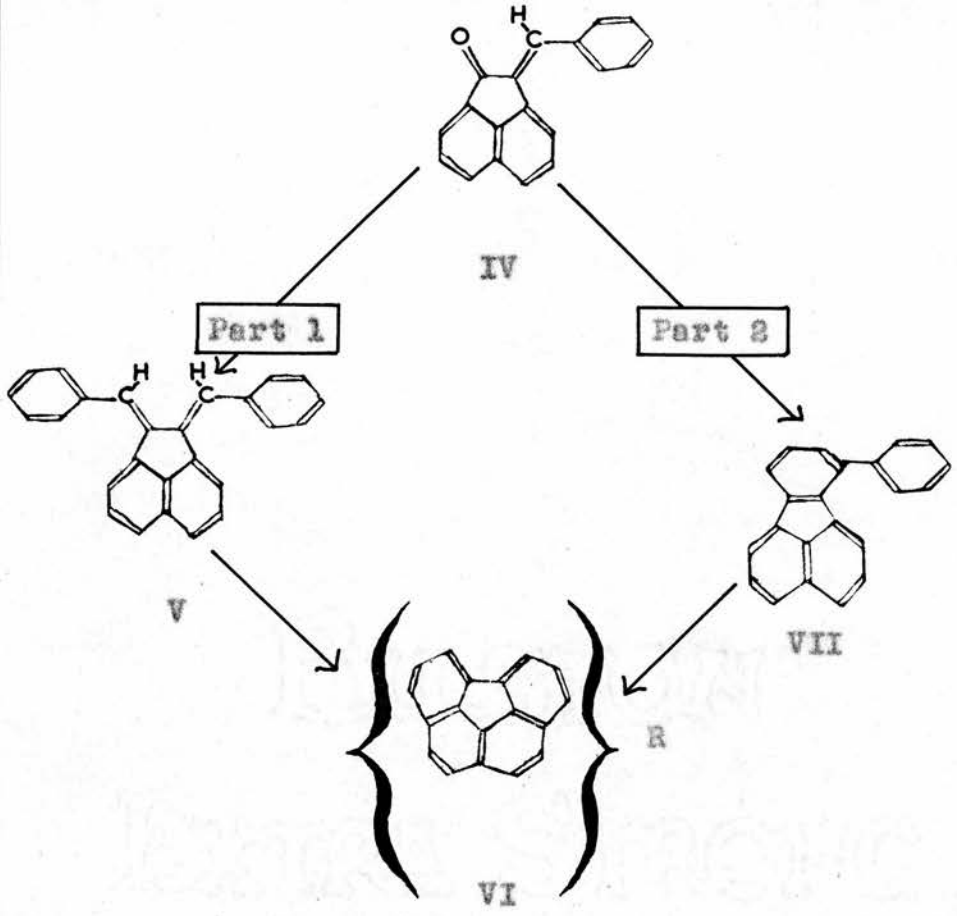
IV

To overcome this difficulty, it was decided to use a derivative which could not dimerise, and 7-benzylideneacenaphthene-8-one (IV) was selected, as it is readily prepared from acenaphthene-8-one (III).

7-Benzylideneacenaphthene-8-one (IV) would be expected to exhibit the reactivity characteristic of its α:β-unsaturated ketonic grouping, and this was partially confirmed by the formation of a keto-chloride, and by reduction and hydrogenation experiments, though this work, and the reaction with diphenylketene, showed that the aromatic nucleus had modified some of the α:β-unsaturated ketonic properties.

The α:β-unsaturated ketonic nature of 7-benzylideneacenaphthene-8-one (IV) suggested two distinct paths along which investigations could be carried out. Firstly, syntheses involving derivatives of 7:8-dibenzylideneacenaphthene (V) were carried out in order to obtain molecules from which 2:13-benzfluoranthene (VI) or its congeners might be formed. The results of some of this work were

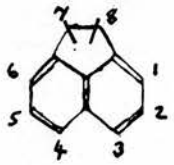
both unexpected and interesting (Part I of this Thesis). Secondly, condensation experiments were carried out to form several derivatives of 10-phenylfluoranthene (VII), again with the hope of ring-closures being affected to form 2:13-benzfluoranthene (VI) derivatives (Part II of this Thesis).



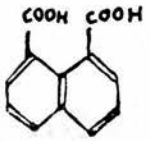
Coronindene

I

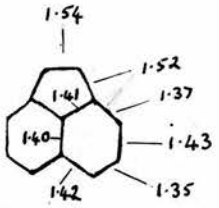
It is advantageous at this point to give a short description of the chemistry of the principal parent compounds involved; acenaphthene, acenaphthylene, acenaphthene-8-one, 7-benzylideneacenaphthene-8-one, fluoranthene, 10-phenylfluoranthene, and the diarylidene- and dialkylidene-acenaphthenes.



VIII



IX

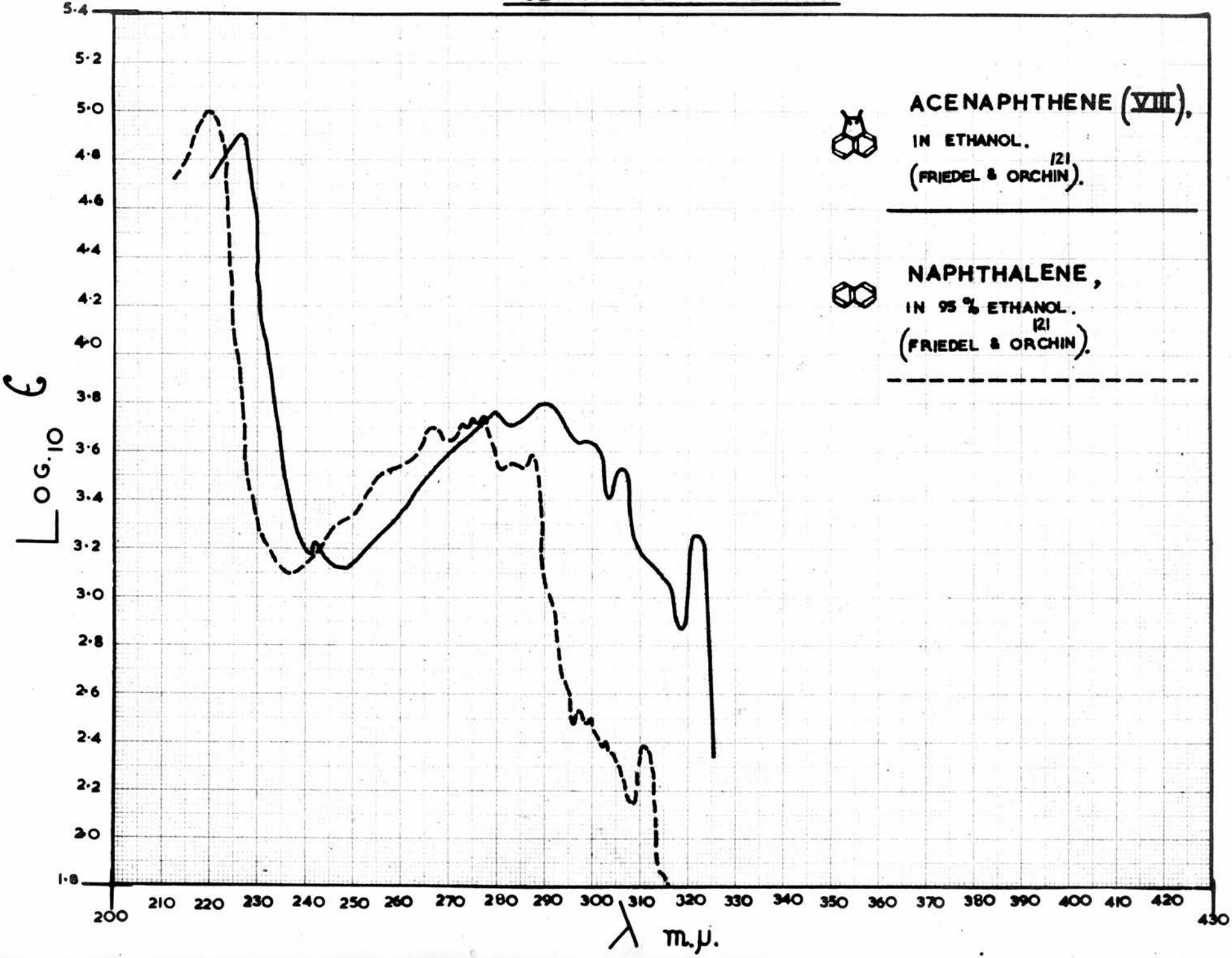


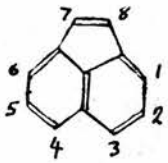
VIIIA

The chemistry of acenaphthene (VIII) is too well known to be detailed here, but can be summarised as follows: the methylene groups of the 7 and 8 positions have a high electron density, and therefore easily lose electrons and the molecule becomes oxidised to naphthalic acid (IX). The high electron density on the 7 and 8 positions also causes movement of electrons into the aromatic rings which are activated in the 1 (or 6) and 3 (or 4) positions, just as the ortho and para positions of a phenyl ring are activated by an alkyl side chain (see references). [4-18]

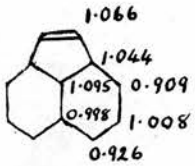
Modern techniques have led to the preparation, from molecular orbital theory (Lumbroso) [20], of diagrams showing the distribution of electronic charge in acenaphthene, and by means of X-ray crystallography, diagrams of the structure of acenaphthene (VIIIA) have been prepared (Kitaigorodskii, [22,23,24] Ehrlich). [111] The ultra-violet spectra of acenaphthene (VIII) and of naphthalene, which it resembles, are shown on p. 5.

ULTRA-VIOLET SPECTRA





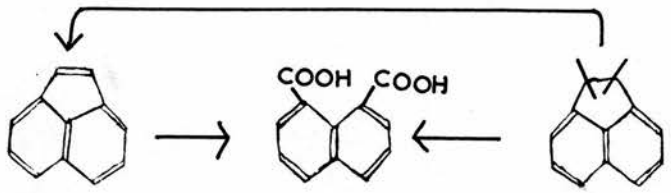
X



XA

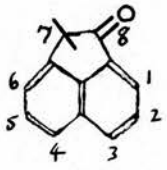
This compound is closely related to acenaphthene (VIII), from which it was first isolated and from which it can be readily prepared[25-27,35], and its structure can be proved by its synthesis from acenaphthene or, as in the case of acenaphthene, by oxidation to naphthalic acid (IX). The distribution of electronic charge on the acenaphthylene (X) molecule has been calculated by Pullman et alia[21] from molecular orbital theory and is shown above (XA), but no X-ray data is yet available in the literature for this compound.

Acenaphthylene (X) forms bright lemon yellow plates, the colour of which proved to be a very useful characteristic of compounds containing an acenaphthylene nucleus. The ultra-violet spectra of acenaphthylenes are also characteristic, and that of acenaphthylene[21,185] is shown on p. 10 . The most striking chemical properties of acenaphthylene are those imparted by the 7-8 double-bond, which enables it to polymerise[182-184] and react as an active dienophile[29,77,78,81]. Further details of the chemistry of acenaphthylene[14,30,31] are available in the literature.



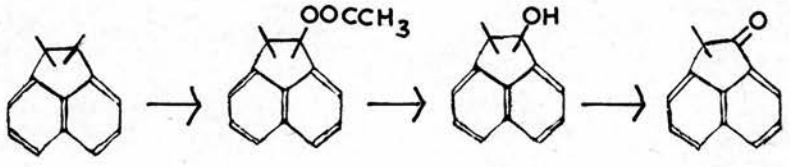
X IX VIII

Acenaphthene-8-one (III)



III

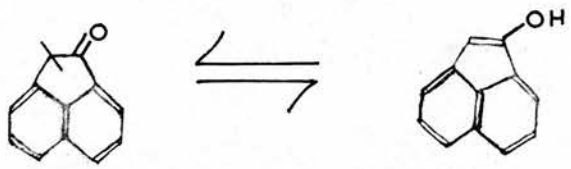
Several methods for the preparation of acenaphthene-8-one (III) have been discovered[15,19,33,36,38], but the most useful is that of Fieser and Cason[39,40], which utilises lead tetracetate oxidation of acenaphthene (VIII) to acenaphthenyl acetate (XII), followed by hydrolysis of this to acenaphthene-8-ol (XIII) and then oxidation to acenaphthene-8-one (III) using chromic anhydride.



VIII XII XIII III

The reactive part of the acenaphthene-8-one (III) molecule is the $-CH_2-CO-$ group, the carbonyl part of which gives normal ketonic reactions forming an oxime[41], and a 2:4-dinitrophenylhydrazone. Enolisation also occurs, though the free enol form, 8-hydroxyacenaphthylene (XIV), has not yet been

isolated, and the lack of yellow colour in neutral solution suggests that the enol can usually only be present in small quantities. The ultra-violet spectrum of acenaphthene-8-one (III) is shown together with that of acenaphthylene (X) on p. 10.

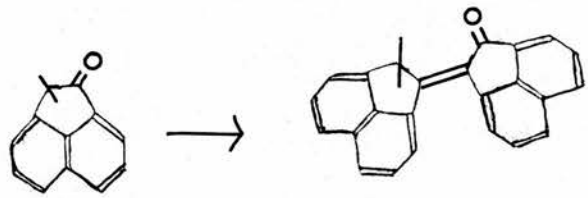


III XIV

Chemical evidence of the formation of an enolate in alkaline solutions is found in the coupling of acenaphthene-8-one with diazonium salts in alkaline solutions[46], and in its acetylation in the presence of pyridine and cold acetic anhydride[47,48]. The evolution of hydrocarbon gases when acenaphthene-8-one is treated with Grignard reagents also[49] shows the existence of the enolate.

The presence of the methylene group can be shown by the formation of an isonitroso and an anisal derivative[42-45], and the very ready formation of other arylidene and similar derivatives by the action of, for instance, aldehydes in the presence of alkali[37,43-45,51,50].

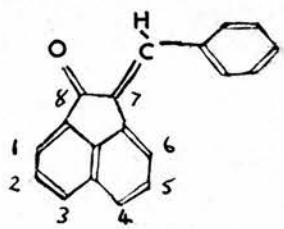
From the point of view of the present work, the formation of arylidene derivatives is important, especially the self-condensation of acenaphthene-8-one (III), in the presence of alkali, to form a dimer, bisacenaphthylidenone (XV)[223,238].



III XV

This reaction occurs so readily that many other base catalysed reactions are masked by it and bisacenaphthylidenone (XV) occurs as a byproduct and impurity from many reactions involving acenaphthene-8-one (III). Failures to condense acenaphthene-8-one with benzylideneacetone (Michael reaction)[52,53], diethyl succinate (Stobbe reaction)[54], ethyl sodium formyl acetate[228], and cyanoacetal[228] can be attributed to this formation of bisacenaphthylidenone (XV). A derivative of acenaphthene-8-one (III) which does not undergo self-condensation was therefore required for the present work, and 7-benzylideneacenaphthene-8-one (IV) was chosen because of its ready availability, ease of purification and stability.

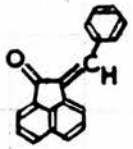
<u>7-Benzylideneacenaphthene-8-one (IV)</u>



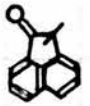
IV

7-Benzylideneacenaphthene-8-one (IV), which in theory should form a cis and a trans isomer, is prepared by the action of benzaldehyde on

ULTRAVIOLET SPECTRA



7-BENZYLIDENEACENAPHTHENE-8-ONE (IV),
IN ETHANOL.



ACENAPHTHENE-8-ONE (III),
IN ETHANOL,
IN CHLOROFORM.

ACENAPHTHYLENE (X),
IN HEPTANE
(PULLMAN et alia[21]).

$\log_{10} \epsilon$

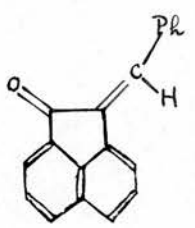
5·4 5·2 5·0 4·8 4·6 4·4 4·2 4·0 3·8 3·6 3·4 3·2 3·0 2·8 2·6 2·4 2·2 2·0 1·8

200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430

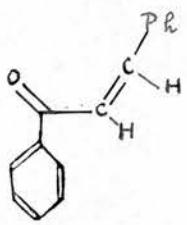
λ m.μ.

acenaphthene-8-one (III) in the presence of a trace of alkali[51,55,56] (see p. 172), and has been known since the nineteenth century, but has not been widely used for synthetic researches.

Chemically 7-benzylideneacenaphthene-8-one is an α:β-unsaturated ketone (IVA), like chalkone (XVI), and the interaction of the carbonyl and olefinic groups of the chalkone system in IV was shown by the lack of normal ethylenic properties. Thus,



IVA



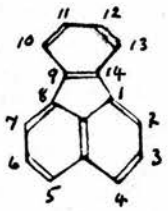
XVI

reduction of the double bond was found to be very difficult (P. 157), and decolourisation of bromine was found only to occur slowly (p. 255).

There is also positive evidence for the α:β-unsaturated ketonic properties of 7-benzylideneacenaphthene-8-one in the occurrence of Michael type condensations[57] which had previously been observed, but not studied systematically (p. 106). On the other hand, the differences between the behaviour of chalkone and of 7-benzylideneacenaphthene-8-one were demonstrated by the incompleteness of the bond rearrangements produced by the action of phosphorus pentachloride and hydrochloric acid on the latter (p. 145), and by the addition of diphenylketene to the ketonic double-bond of 7-benzylideneacenaphthene-8-one rather than to the α:β-unsaturated system as

a whole. This signifies that the aromatic nucleus has considerably altered the α:β-unsaturated ketonic properties of 7-benzylideneacenaphthene-8-one (see p. 160). The ultra-violet spectrum of this compound is shown on p. 10.

Fluoranthene (II)

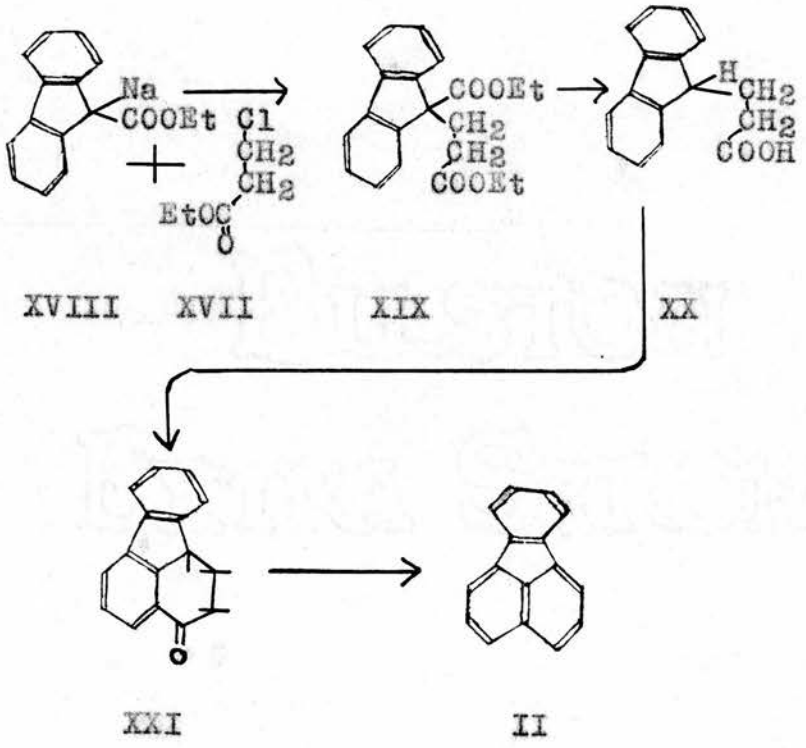


II

Fluoranthene (II) was first isolated almost simultaneously, though independently, by Goldschmiedt[59] and by Fittig and Gebhard[60] in 1877. Goldschmiedt isolated a compound which he named 'idryl', from the stupp fat obtained during the preparation of mercury from the cinnabar mined at Idria in Northern Italy, while Fittig and Gebhard isolated the hydrocarbon, which they named 'fluoranthen', from coal tar, of which it forms some 0.6%, and which is the principal source of the substance.[33,64,66,120] In recent years claims have been made that fluoranthene has been found along with other hydrocarbons in the bodies of certain types of barnacle (tetraclita squamosa rubescens), whither it may have passed from oil residues.[61,62]

Originally fluoranthene was assigned the formula $C_{15}H_{10}$ and various structures were proposed for it, until in 1929 the correct formula ($C_{16}H_{10}$) and structure for fluoranthene (II) were assigned by

von Braun[63] and Anton who devised the first synthesis of the substance. Von Braun and Anton used the method of synthesis shown in Scheme A below: interaction of the ester of β-chloropropionic acid (XVII) and the sodium derivative of fluorene-9-carboxylic ester (XVIII) formed the 9-carbethoxylate of β-9-fluorenylpropionic ester (XIX), which on hydrolysis and decarboxylation yielded β-9-fluorenylpropionic acid (XX). The acid on ring-closing formed 4-keto-1:2:3:4-tetrahydrofluoranthene (XXI). Clemmensen reduction of this last compound followed by dehydrogenation with red hot lead oxide yielded fluoranthene (II).



XVIII XVII XIX XX

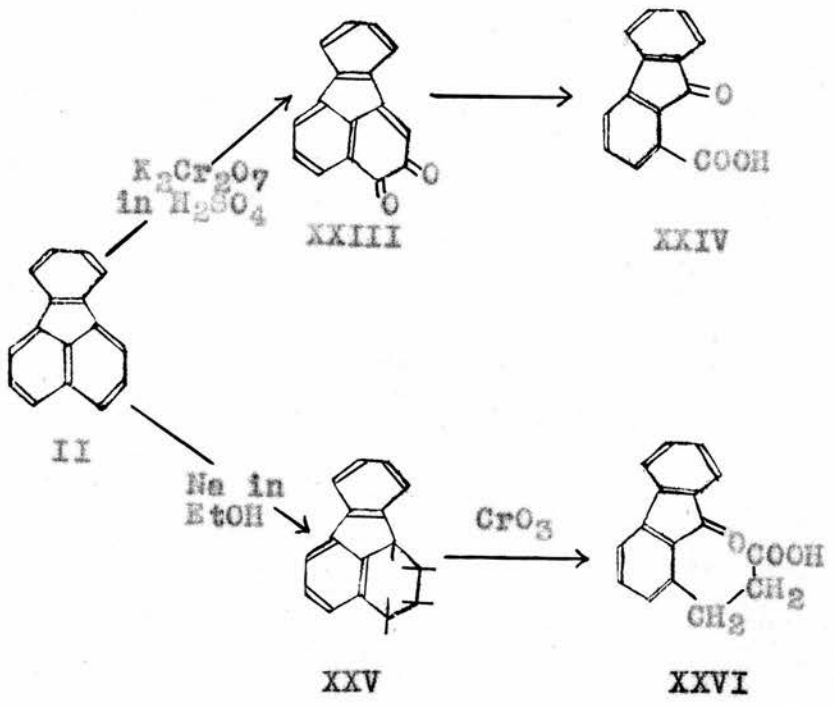
XXI II

Scheme A

This structure for fluoranthene was evolved and confirmed by Fittig and Gebhard[64], Fittig and Liepmann[65], von Braun and Anton[63], and Kruber[66] by the

oxidation of fluoranthene itself, and of tetrahydrofluoranthene (XXV), to form the known acids XXIV and XXVI (Scheme B).

Details of the properties of fluoranthene can be found in one of the standard textbooks[67], and in the literature[68], however a brief outline of the

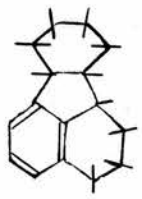


II XXIII XXIV XXV XXVI

Scheme B

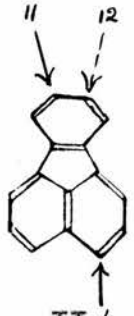
properties of the substance is included here.

The oxidation of fluoranthene (II) to form fluoranthene-3:4-quinone (XXIII) and the acidic degradation products XXIV and XXVI has already been mentioned[63-66]. Reduction to 1:2:3:4-tetrahydrofluoranthene (XXV) has also been mentioned but by further reduction, using catalytic hydrogenation methods[69], it is possible to form decahydrofluoranthene (XXVII) and perhydrofluoranthene (XXVIII).

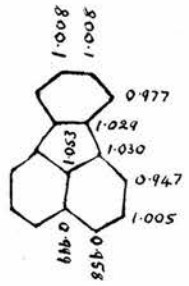


XXVII

XXVIII



II



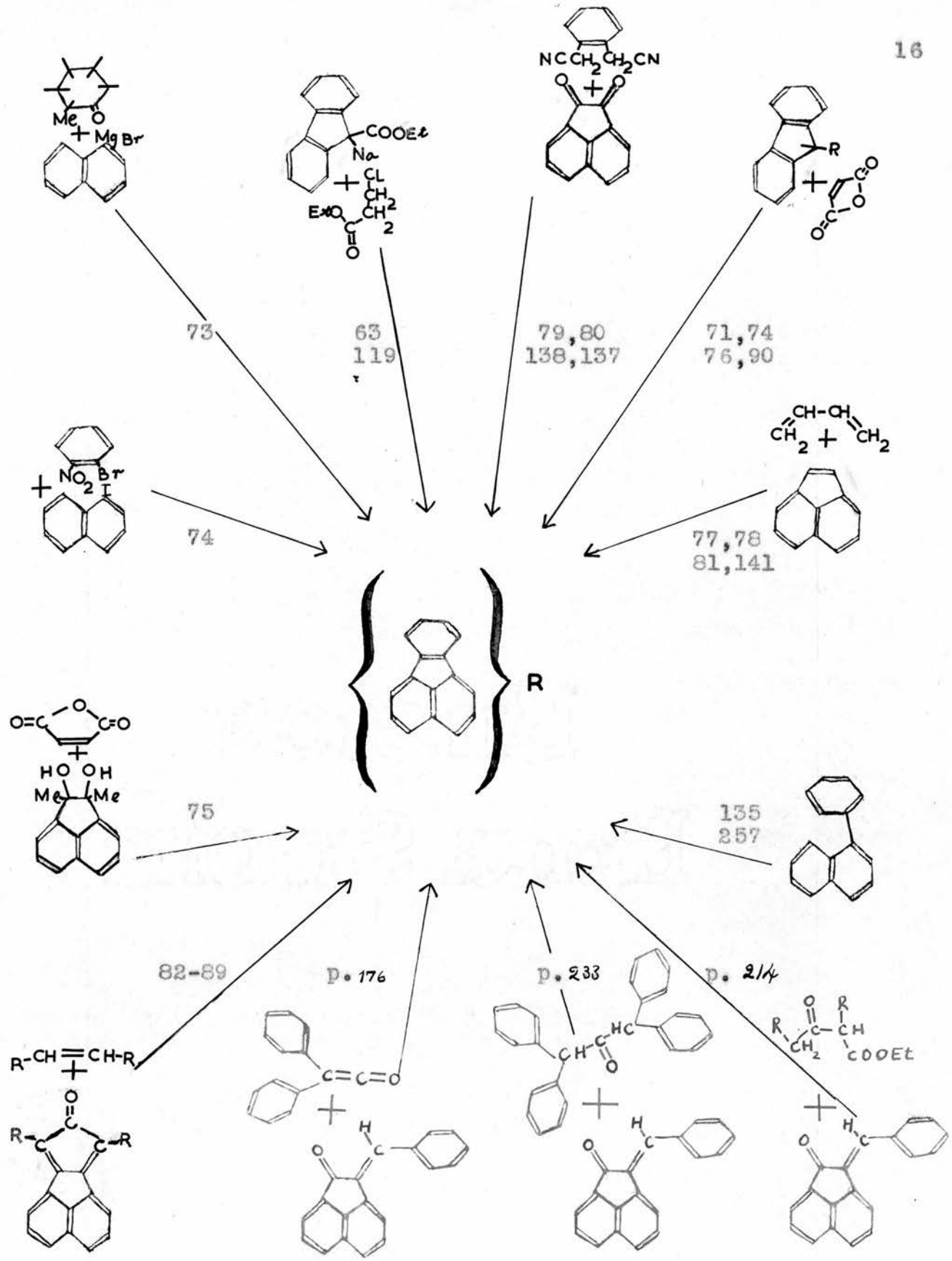
IIA

The active positions in the fluoranthene molecule are the 4, 11 and 12 positions, and it is here that substitution occurs. The '4' position is the most active and bromination, nitration and sulphonation[70] yield mainly '4' monosubstitution products. Acetylation, benzoylation and phthaloylation, however[70,71] also yield the '11' monosubstitution product, and when the fluoranthene is disubstituted, the '12' position is found to have reacted.[72]

X-ray data for fluoranthene are not available, and bond lengths cannot therefore be shown, however, diagrams of the distribution of electronic charge have been calculated from molecular orbital theory,[28,21] and are shown in formula IIA, though it seems difficult to relate these figures to the known chemical properties of fluoranthene. The ultraviolet spectrum of fluoranthene is shown on p. 40.

The syntheses of fluoranthene and its derivatives are too numerous to be described here, but some of them are summarised with reference in Scheme C, which also shows the methods employed in this work to prepare substituted fluoranthenes (shown in red).

Before passing on to the branched and unstable hydrocarbons involved in this work, it should be

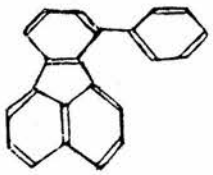


Scheme C

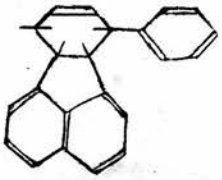
Some types of synthesis of fluoranthene and its derivatives.

noted that these symmetrical aromatic hydrocarbons, fluoranthene, acenaphthene, acenaphthylene and many others besides, show great stability. The very fact that they are found in coal tar,[33] and the frequency with which they are formed in 'red hot tube' reactions emphasises this, leaving some hope that the highly symmetrical aromatic system of coroninden (I) may be synthesised.

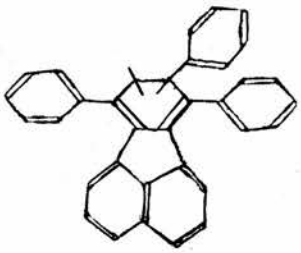
10-Phenylfluoranthene (VII)



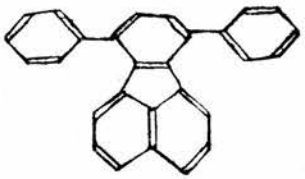
VII



XXXVI



XXXVII

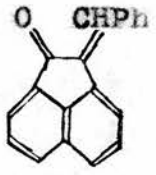


XXXVIII

The preparation of 10-phenylfluoranthene (VII) has not yet been reported in the literature, though Bergmann has prepared 10-phenyl-9:10:13:14-tetrahydrofluoranthene (XXXVI), (and also 10:13-diphenyl-9:10:13:14-tetrahydrofluoranthene), by diene reactions between acenaphthylene and phenylated butadienes[78,81] (see Scheme C p.16), but no dehydrogenation of the tetrahydro derivative was

reported. More complex fluoranthenes, such as 10:13-diphenylfluoranthene (XXXVIII) and 10:11:13-triphenyl-11:12-dihydrofluoranthene (XXXVII) have however been prepared by the use of acecyclone and similar derivatives[82-89], but the reliability of these reactions for determining structure is thrown in doubt because of the high temperatures required over long periods in most though not all such reactions[91].

Diarylidene- and Dialkylidene- Acenaphthenes (XXX)



IV

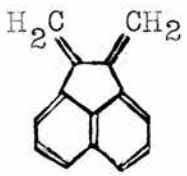
XXX

("=CHR" can be; methylene, ethylidene, propylidene, isobutylidene, isoamylidene, or benzylidene.)

It has been shown how easily a benzylidene group may be attached to an acenaphthene nucleus to form the stable compound 7-benzylideneacenaphthene-8-one (IV). However, to attach two such groups is a much more difficult undertaking and the product is not a stable compound. This appears to be generally true of the preparation of the dialkylidene- and diarylidene- acenaphthenes (XXX). The butadiene part of these molecules seems to be activated by the aromatic nucleus[93] and to polymerise readily, so that some of these acenaphthenes are either extremely difficult, or impossible to isolate. Building models of these molecules illustrates a further point, namely, that there is

an overcrowding effect, as well as restricted rotation of the substituents where these are large (p. 35), and the strain which this close packing of the molecule causes may account in part for the difficulty of formation of some diarylidene- and dialkylidene- acenaphthenes.

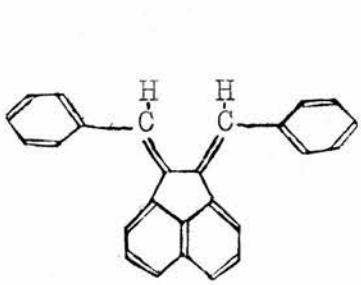
Dialkylideneacenaphthenes



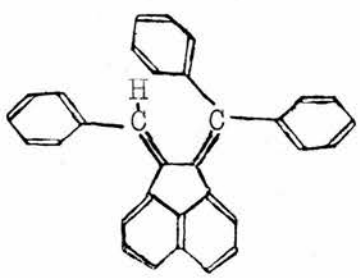
XXXI

Maxim claimed to have isolated 7:8-dimethyleneacenaphthene (XXXI) as well as 7:8-diethylidene-, 7:8-dipropylidene-, 7:8-di-isobutylidene-, 3-bromo-7:8-diethylidene-, and crude 7:8-di-isoamylidene-acenaphthenes.[93-96] Gow unsuccessfully tried to repeat Maxim's method though he obtained XXXI transiently in his synthesis of fluoranthene[97,98,258] (see Scheme C, p. 16 [75]), and he concluded that the compound claimed by Maxim to be XXXI was in fact a polymer (see also[100-102]).

Diarylideneacenaphthenes



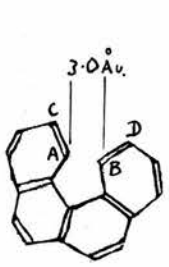
V



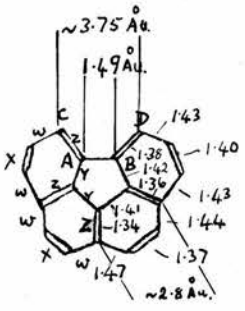
XXXII

The difficulty involved in preparing 7:8-dibenzylideneacenaphthene (V) was shown by J. Staf-

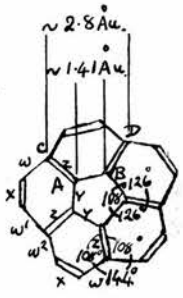
ford, who tried to repeat Maxim's synthesis but was [103,279] [93,94]
unable to obtain more than 1% yields of V, and after trying a further nine methods of preparation [98,100-102,104,105] was only able to improve his yields of V to 4% (p. 26). Stafford also claimed that 7:8-dibenzylideneacenaphthene (V) was rapidly destroyed by ultraviolet light. [128] In the present work 7-diphenylmethylene-8-benzylideneacenaphthene (XXXII) was prepared transiently (p. 55) as a reaction intermediate in the synthesis of a fluoranthene, but the pure substance was not isolated, though a solution and an ultraviolet spectrum were obtained (p. 56).



XXXIV

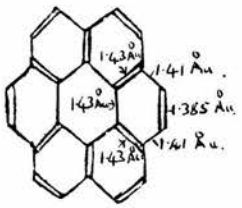


XXXV



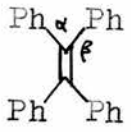
IA

Finally it is appropriate to consider briefly the hypothetical coronindene (I), which resembles coronene (XXXIII) in structure, both being highly symmetrical and compact molecules. The symmetry and compactness of coronene give it very high aromaticity; otherwise expressed, it possesses a very high resonance energy and a perfectly planar form, [99,106,107,113] and hence the molecule is extremely stable (it melts at 438-440° C). [67] Coronindene, therefore, might be expected to show similar high stability and planarity.



XXXIII

Coronindene however would contain a five membered ring, and the effect of this must be considered. In passing from the ring systems of 3:4-benzphenanthrene[109] (XXXIV) to 2:13-benzfluoranthene[110,111] (XXXV) and to coronindene[107] (IA), the gaps AB and CD must be diminished, introducing strain into the molecule. The sources of this strain are twofold.



$\alpha = 111^{\circ}20'$

$\beta = 124^{\circ}20'$

$\gamma = 120^{\circ}$

XXXIX I(B) I(C)

Firstly, a geometric construction of I (IA) based on the assumption that the bond lengths are all the same shows that the valency angles between W^1 and W^2 are substantially larger (144°) than is usual for carbon atoms forming double bonds as in e.g. XXXIX.[108,112] Consideration of XXXV[111] shows that this strain is principally relieved by shortening of the Z bonds, which presumably gain in double bond character,[106,113,114,258] thus favouring the 'spoked' canonical form (shown in XXXV and IA).

Secondly, there is the overcrowding effect[109,115-118], by which the repulsion of the molecule's own too proximate parts forces the atoms, though firmly bound together, to get as far from each other as possible. Thus in 3:4-benzphenanthrene (XXXIV) the molecule is distorted into a helical form and the gap AB in XXXIV and XXXV is much wider than the geometry of the constituent benzene rings would predict. This effect is important as a means of comparing the forces of the normal aromatic bond with the forces maintaining the planarity of the aromatic molecule. In coronindene (IA) this force can find relief by tending to increase the overall diameter of the molecule by lengthening the W and X bonds, or by the adoption of a 'fluted' form of molecule (IC) or by lengthening the Z bonds, the two latter possibilities however, would tend to be prevented by the increased strain produced by increasing the angle between the valencies W^1 and W^2. The adoption of a 'coronal' form (IB) to decrease the angle between these bonds and form a strainless molecule would increase overcrowding and would seem unlikely especially in view of the known planarity of coronene[107] and 2:13-benzfluoranthene[110,111], and the fact that the thickness of the latter[111] seems to preclude resonance between opposite 'coronal' forms.

Thus coronindene (I) would seem likely to be a stable, planar molecule once the strains involved in formation have had time to disperse throughout the molecule, but its formation would seem

likely to be difficult. How far these ideas are correct presents a problem that can only be solved by experiment.

DISCUSSION

PART I

SYNTHESES INVOLVING THE CONGENERS

OF 7:8-DIBENZYLIDENEACENAPHTHENE

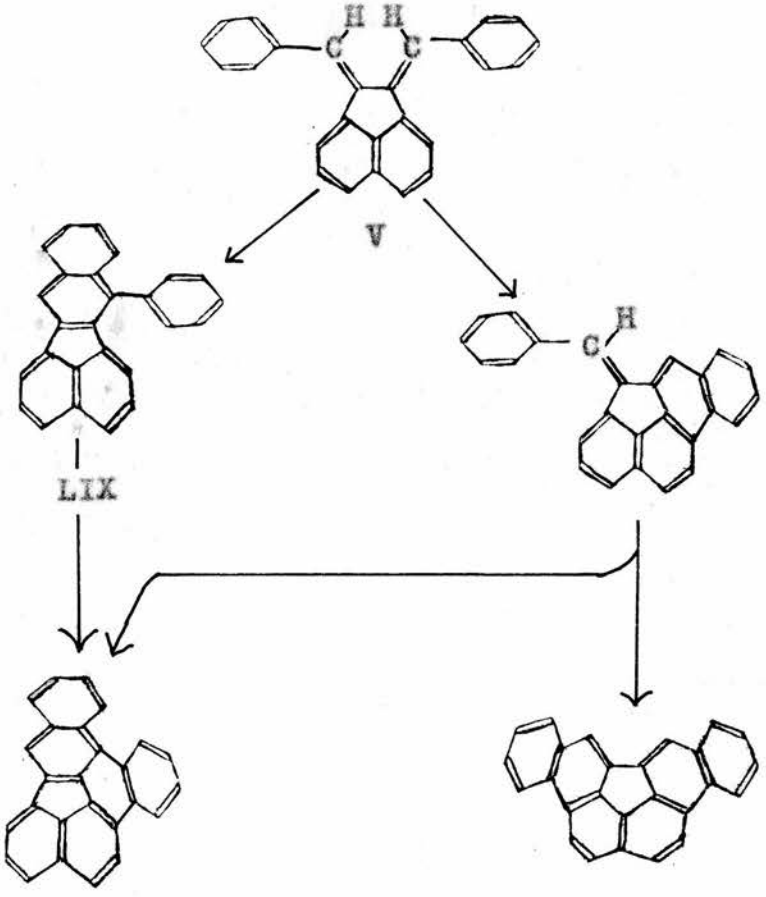
Section I

The Use of Diphenylketene

The Action of Diphenylketene on 7-Benzylideneacenaphthene-8-one

The aim of this part of the work was to synthesise substituted 7:8-diarylideneacenaphthenes and thence polycyclic aromatic hydrocarbons, especially fluoranthenes, which might be suitable intermediates for the preparation of coronindene (I) and

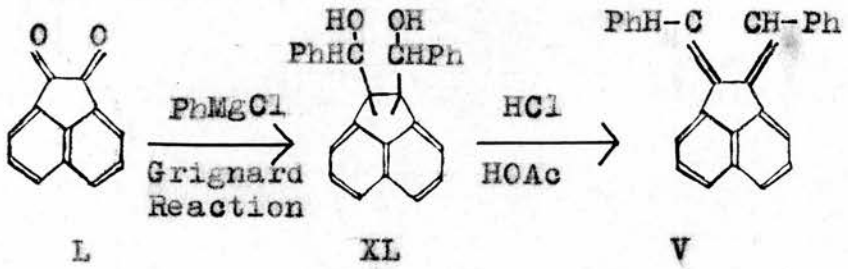
Braet. p. 168



Scheme D

its derivatives.

As an example the products hypothetically obtainable from 7:8-dibenzylideneacenaphthene (V) are shown above in Scheme D. 7:8-Dibenzylideneacenaphthene (V) has been synthesised by Maxim[94] by the dehydrating action of conc. HCl in glacial acetic acid on 7:8-dihydroxy-7:8-diphenylacenaphthene (XL) as in Scheme E, but Maxim's description of the compound as forming fine microscopic yellow orange



L XL V

Scheme E

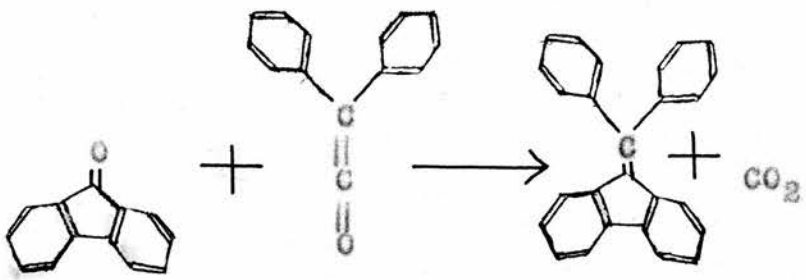
crystals of melting-point about ('vers') 142°C. leads one to suspect that it was impure. Later work by J. Stafford[103,279] at Cambridge emphasised the difficulty of preparing this compound as this worker was only able to obtain 1% yields by Maxim's method. Many dehydrating agents were tried: glacial acetic acid, HCl in glacial acetic acid by both Maxim's[93,94] and Beschke's[100] methods, iodine in glacial acetic acid, aluminium chloride in carbon disulphide and in benzene, conc. sulphuric acid at 0°C., potassium hydrogen sulphate, distillation from calcium oxide, and decomposition of the urethane, but the best yield was 4% of a compound which formed pale yellow crystals, melting at 163°C., which were photosensitive especially to ultra-violet light, and had a

striking purple fluorescence not mentioned by Maxim. Stafford obtained several other products from the reaction and pointed out the possibility of the formation of geometric isomers of 7:8-dibenzylideneacenaphthene (V). The difference between Maxim's and Stafford's descriptions of the compound confirms that that obtained by Maxim was not pure 7:8-dibenzylideneacenaphthene (V).

The isolation of 7:8-dimethyleneacenaphthene, 7:8-diethylideneacenaphthene, 7:8-dipropylideneacenaphthene, 7:8-di-isobutylideneacenaphthene, 3-bromo-7:8-diethylideneacenaphthene, and in the crude state 7:8-di-isoamylideneacenaphthene, has also been claimed by Maxim[93-95], all being obtained by the same type of reaction as that shown in Scheme E for 7:8-dibenzylideneacenaphthene (V). Doubt, however, is cast on the identity of some of these products as their melting-points appear not to be sharp, and Gow, though able to obtain 7:8-dimethyleneacenaphthene (XXXI) transiently, as is proved by his synthesis of fluoranthene (II)[75,258], was quite unable to isolate the compound, and indeed Maxim's own description of his product as being nearly insoluble in all organic solvents, which distinguishes it from his description of the higher homologues which he claimed to have obtained, contradicts later knowledge of this type of compound[103,279] (p. 58), and it would seem that his compound was probably a polymer. Evidence has also been put forward by Criegee, Kraft and Rank[97] that the acenaphthene glycols used by Maxim were impure.

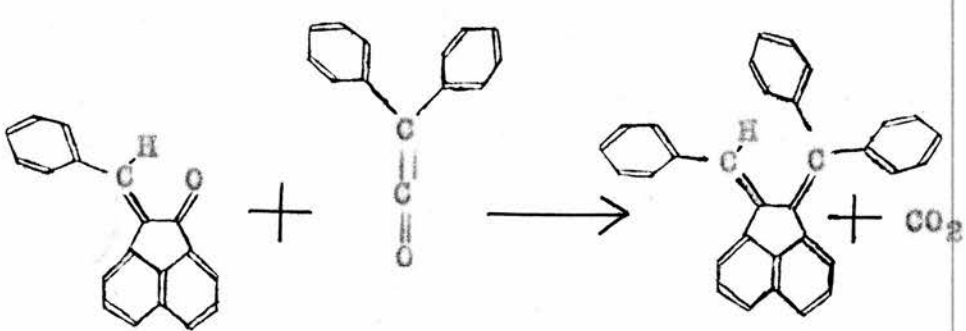
In conclusion, it would seem likely that dialkylidene - and diarylidene - acenaphthenes are unstable and very difficult to prepare, and other methods of preparation would be advantageous if they are to be used for the synthesis of substituted fluoranthenes.

Staudinger in his studies on ketenes and especially diphenylketene (XLII) discovered a reaction which seemed likely to be useful to this end. The interaction of this ketene and some ketones affords a diphenylmethylene derivative by the elimination of CO_2 and from fluorenone[179] (XXIX), for instance, 9-diphenylmethylenefluorene (XXII) is obtainable.



XXIX XLII XXII

As diphenylketene (XLII) is the most readily handled of the ketenes, it was decided to try the effect of this on 7-benzylideneacenaphthene-8-one (IV), in the hope of synthesising 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII).



IV XLII XXXII

The preparation of diphenylketene (XLII) was attempted by one of Staudinger's methods,[128,132 (see also 131,127)] namely, by the action of quinoline on diphenylacetyl chloride, but this was found to be unsatisfactory. however the method developed by Smith and Hoehn,[130] who obtained diphenylketene by heating the diazo derivative of benzil monohydrazone[129] in high vacuum was found to be satisfactory, and was employed throughout the experiments.

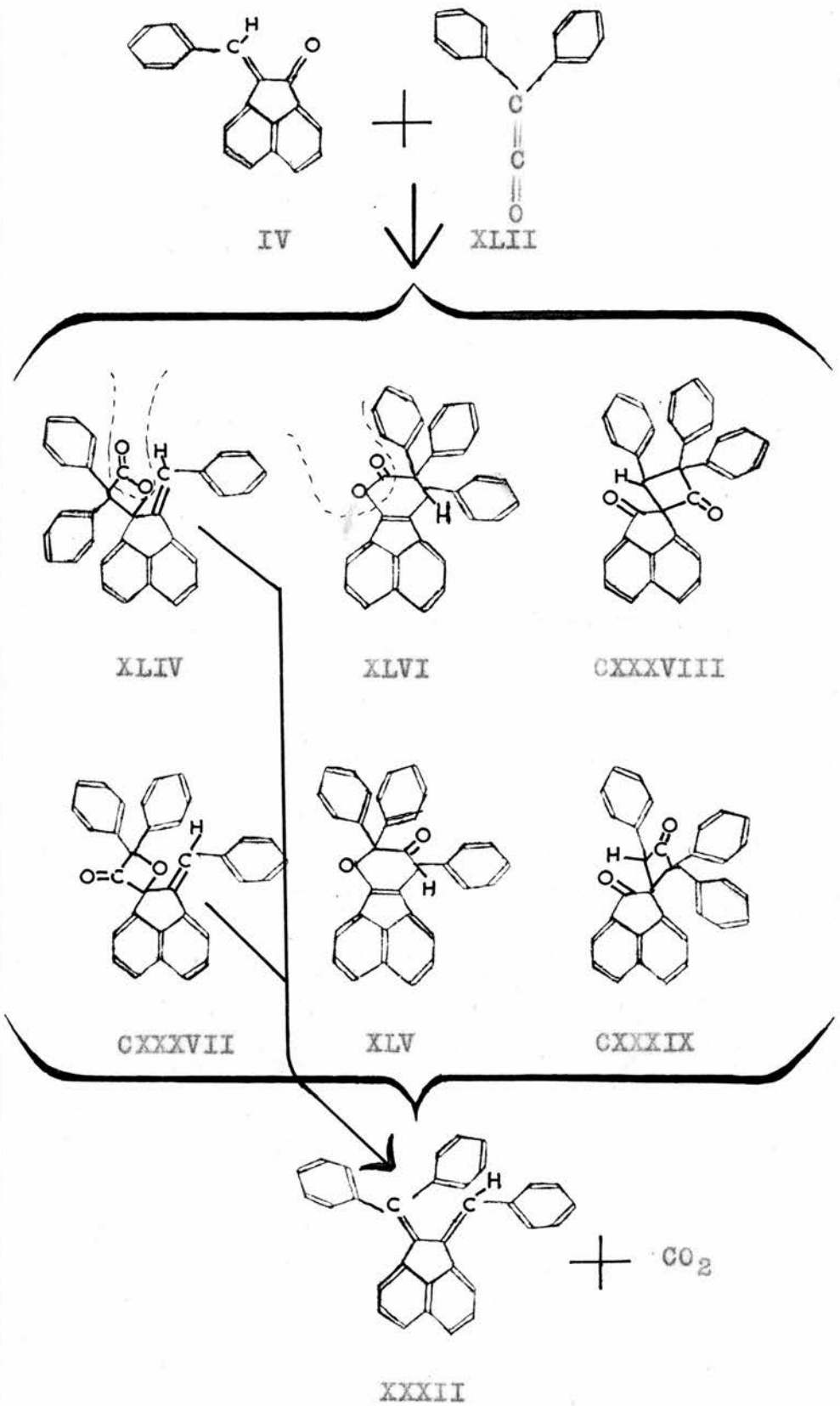
7-Benzylideneacenaphthene-8-one[51] (IV, 2·0 gm.) was heated with an equal weight of the ketone, in an atmosphere of nitrogen at 115-140°C. for 140 minutes. The products were extracted with ether and yielded 0·6 gm. of unchanged 7-benzylideneacenaphthene-8-one (IV, 30%) together with 0·4gm. of a yellow crystalline compound which when purified melted at 243-5°C. After further, but unsuccessful attempts at crystallisation, the residues were passed through a column of alumina and eluted with petrol-benzene mixture yielding a red and a yellow band. The red band afforded pale yellow plates which when purified melted at 273-4°C. (Compound 'A') and which gave a pale yellow solution with a striking purple fluorescence (a red colour was found later to be associated with an intermediate, see p. 55), while the yellow band of the benzene-petrol eluate yielded canary yellow prisms of melting-point 243-5°C. (Compound 'B'), identical with the yellow crystals obtained earlier by direct crystallisation. Further elution with acetone produced a yellow band from which some starting

material was obtained, and 20 mg. of pale orange prisms, melting at 174-6°C. with decomposition (Compound 'C'), which were purified by crystallisation from acetone - benzene to separate them from some Compound 'B' which had also been eluted. Lastly, with acetone, a red eluate was obtained, which yielded a few milligrammes of very fine red needles of M.P. 296-302°C., (Compound 'D'), which started to sublime at 290°C. Unfortunately there was not sufficient of this compound for it to be analysed.

To identify these compounds we shall first look at the theoretically likely products, and then at the relevant substances claimed or obtained by Maxim and Stafford.

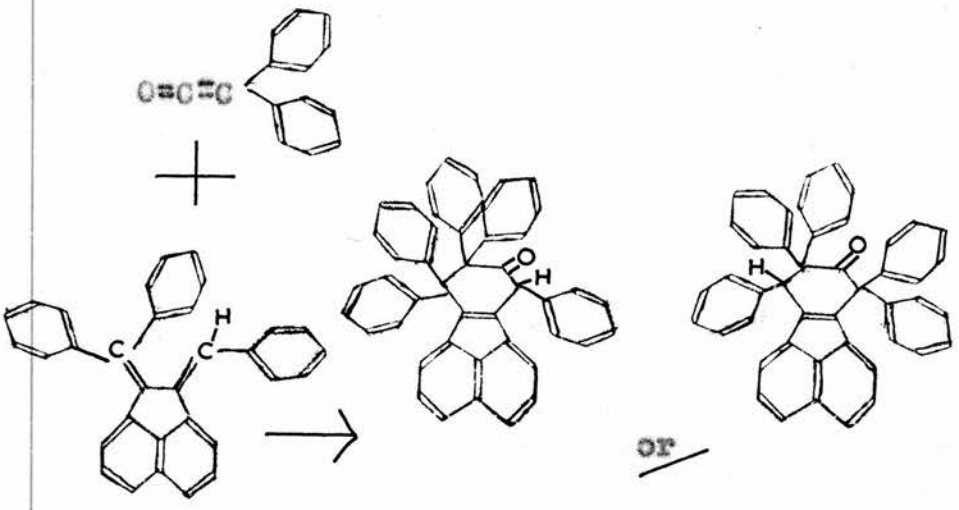
The reaction between diphenylketene (XLII) and 7-benzylideneacenaphthene-8-one (IV) is essentially a diene reaction, with the ketene acting as a dieneophile. In theory, therefore, any of the isomers XLIV, XLVI, CXXXVIII, CXXXVII, XLV, and CXXXIX might initially be formed.[123,124] Staudinger has shown, however, that of these only XLIV and XLVI participate in this type of reaction, and only these can readily split off CO_2 to form XXXII. It will be assumed for the present that the reaction intermediate is in fact the β-lactone XLIV. The reactions that would be consequent upon the initial formation of the δ-lactone XLVI are discussed on p.61.

There are further likely reaction products. As an excess of diphenylketene was present during the reaction, there is the possibility of this

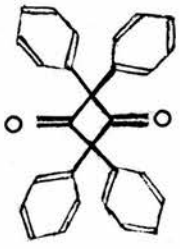


reacting with XXXII, which is itself a diene, to produce XLVII or XLVIII. Moreover, diphenylketene can itself polymerise to form 2:2:4:4-tetraphenyl-cyclobutane-1:3-dione (XLIX), (this structure is used throughout this Thesis though later work with

other ketenes suggests it may not be correct[168,227]), and another compound, of M.P. 176°C., mentioned by Staudinger as being of unknown composition but probably a polymer of diphenylketene[260] (XLII). In addition, 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) is a butadiene, and as such is liable to polymerise or form a dimer as suggested by Gow[261] for 7:8-dimethyleneacenaphthene (XXXI).



XXXII XLII XLVII XLVIII



XLIX

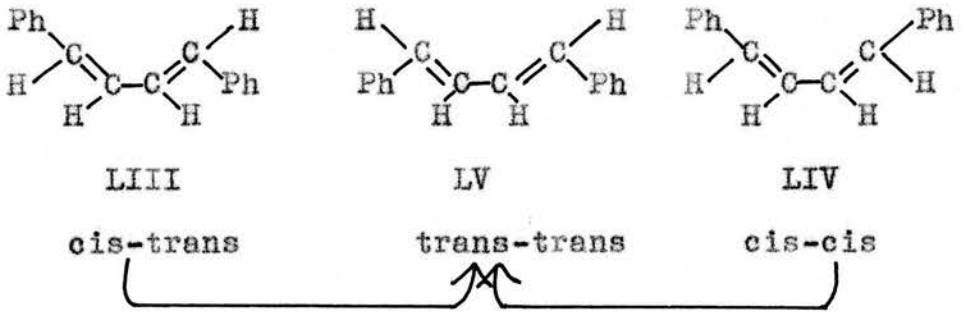
This list of the theoretically likely products of the reaction between IV and XLII should not, however, be restricted to these distinct compounds, as there are also numerous possibilities of optical isomerism, while compound XXXII, amongst others, is capable of geometric isomerism which was more important, especially in the case of the principal

expected product XXXII.

Stafford[281] argued that in the case of 7:8-dibenzylideneacenaphthene (V) three isomers were possible, basing his argument on the known isomerides of distyryl[133] LIII, LIV, LV, and suggested that the isomers LVI, LVII, LVIII, would be formed with 7:8-dibenzylideneacenaphthene (V). Stafford isolated five different compounds from his synthesis of V. Two of these contained oxygen, but the other three compounds, A', B', C', had similar analyses and infra-red spectra corresponding to 7:8-dibenzylideneacenaphthene (V, $C_{26}H_{18}$), and he concluded that these were the three isomers LVI, LVII, and LVIII, and probable formulae were alloted to the compounds by analogy between some of their physical properties and those of the corresponding distyryls.

Stafford's[279] compound A' formed yellow needles of M.P. 163-163·5°C. which gave a solution with a striking purple fluorescence, and the compound decomposed on exposure to ultra-violet light to give a red resin from which the original hydrocarbon could not be recovered. On hydrogenation this compound took up two moles of hydrogen and was assumed to be the cis-trans form LVI, because of the similarity to cis-trans distyryl LIII, which is rapidly changed by light into LV, the trans-trans form. (cp. the polymerisation of styrene by light[134,262]).

Stafford's[279] second compound B' formed yellow crystals difficultly soluble in cold benzene, and of melting-point 242°C. This compound could not be satisfactorily catalytically hydrogenated, and

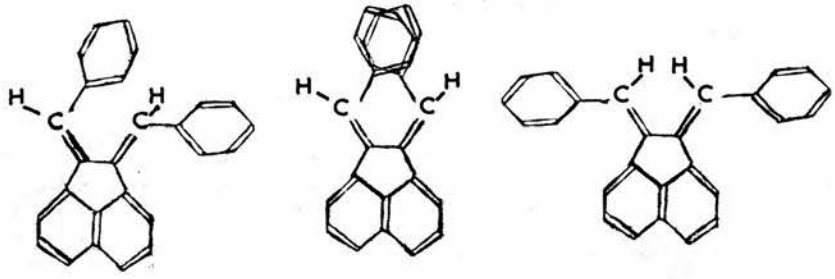


LIII cis-trans | LV trans-trans | LIV cis-cis

Light, gradually

Labile liquid, can be preserved in dark for a limited period.	Stable form, colourless crystals with blue fluorescence, M.P. 147-8°C.	Yellow crystals, M.P. 70-70·5°C.

133 266,267 133

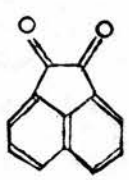


LVI cis-trans | LVII cis-cis | LVIII trans-trans

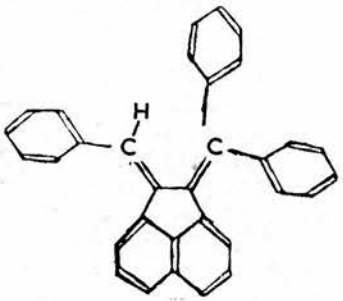
Yellow crystals, blue fluorescence, M.P. 163°C.	Yellow crystals, M.P. 242°C. (probably).	Yellow crystals, M.P. 327°C. (probably).

as it was decomposed by molten camphor, and only slightly soluble in benzene and other solvents, its molecular weight could not be determined accurately. This compound was assigned the probable structure of the cis-cis form (LVII).

The third compound C'[279] formed yellow, sparingly soluble crystals of M.P. 327°C. which could not be satisfactorily catalytically hydrogenated, and which did not yield acenaphthenequinone (L) on ozonolysis. This compound was considered most probably to be the trans-trans form (LVIII). Stafford's assignation of formulae to A', B' and C' will however be commented on at a later stage (p.60).



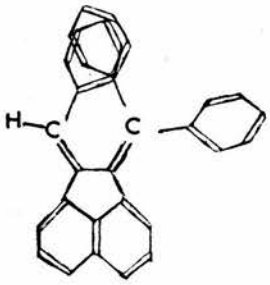
L



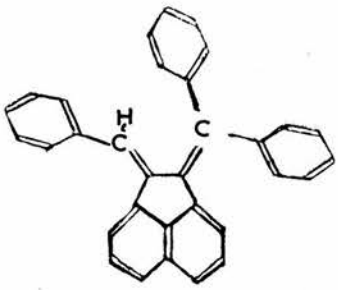
XXXII

The application of these considerations to 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII), causes two points to emerge. Firstly, as the diphenylmethylene group in XXXII is symmetrical, only two isomers can be formed, a cis (LX) and a trans (XXXII) form, and secondly, a study of models shows that the cis form (LX) is unlikely to occur as the phenyl groups interfere sterically, and therefore any 7-benzylidene-8-diphenylmethyleneacenaphthene which is formed is likely to be in the trans form XXXII.

Models also suggest that 7:8-dibenzylideneacenaphthene (V) is not likely to form a cis-cis isomer for here again the phenyl groups interfere considerably despite their free rotation. This is discussed on p.59, 60.



LX



XXXII

In Table I there is a list of the theoretical analyses of the substances discussed as being likely products from the interaction of diphenylketene (XLII) and 7-benzylideneacenaphthene-8-one (IV), and for comparison the analytical results actually obtained for the products of the reaction are listed alongside.

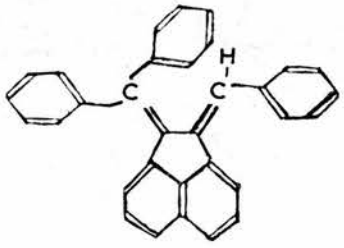
From the analytical results it seemed likely that compound A, melting-point 273-4°C., was 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII). The percentage of oxygen in compound B, melting-point 243-5°C., suggested that this was a relatively large molecule, and its analysis accorded with those of the pentaphenyl-10:11:12:13-tetrahydrofluoranthenones XLVII and XLVIII, while the analysis of compound C, melting-point 174-6°C., suggested that this was a dimer of diphenylketene, a conclusion supported by Staudinger's finding that a polymeric

compound of unknown composition melting at 176°C. was produced by heating diphenylketene. We shall now consider these substances separately and assess whether their properties conform to the above conclusions.

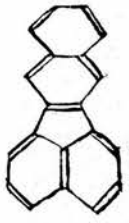
Table I, Analyses

Theoretical Product	Theoretical Analysis			Actual	Actual Analysis		
	C%	H%	O%	Product	C%	H%	(O%)
XLIV CXXXVII CXXXIX $C_{33}H_{22}O_2$	88.0	4.9	7.1				
CXXXVIII, XLVI, XLV $C_{33}H_{22}O_2$	88.0	4.9	7.1				
XXXII $C_{32}H_{22}$	94.5	5.5	0.0	A	94.6	5.06	0.34
Polymer, Dimer	94.5	5.5	0.0				
XLVIII $C_{46}H_{32}O$	92.0	5.4	2.7	B	91.8	5.7	2.5
XLVII $C_{46}H_{32}O$	92.0	5.4	2.7	B	91.8	5.7	2.5
XLIX $C_{28}H_{20}O_2$	86.6	5.2	8.2	C	85.1	5.6	9.3
Polymer of XLII	86.6	5.2	8.2	C	85.1	5.6	9.3
LXIII $C_{32}H_{22}$	94.5	5.5	0.0	A	94.6	5.06	0.34
LXIV $C_{32}H_{20}$	95.0	5.0	0.0	A D	94.6	5.06	0.34

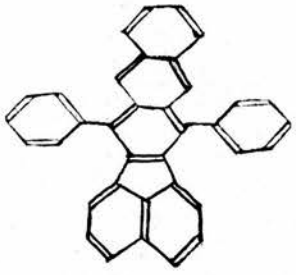
Compound A. This compound, which analysis showed to be a hydrocarbon, formed pale yellow leaflets or rosettes which in solution gave a striking purple fluorescence, thus resembling Stafford's[105,279] compound A. Compound A, however, did not undergo the catalytic hydrogenation which would be expected of a butadiene derivative, despite repeated efforts under various conditions and with different catalysts, and this cast serious doubt on whether this compound was in fact XXXII. As the compound had been



XXXII



LXII

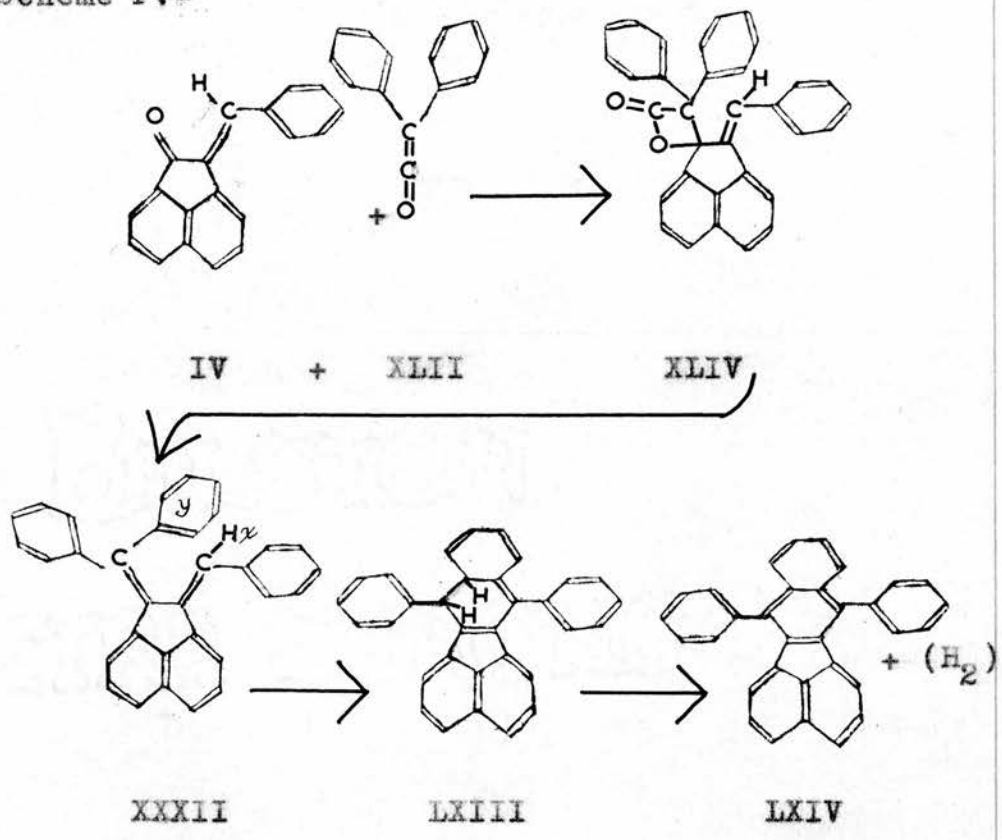


CXL

proved to be stable to ultra-violet light, its ultra-violet spectrum was observed in the hope that this would provide a clue to the structure of the compound. Comparison of this spectrum with those in the literature showed it to be similar in form to those of fluoranthene, its hydrocarbon congeners, and perylene[121] (p.40). Further searching on the basis of this showed that the spectrum was practically identical with that of benzfluoranthene, believed to be 11:12-benzfluoranthene (LXII), discovered by Orchin and Regel,[135-138] and others, and later found in coal tar by Kruber,[32] and also similar to the spectrum of 10:13-diphenyl-11:12-naphthofluoranthene (CXL), which was synthesised by Allen and Van Allen[91] and incorrectly claimed as 10:13-diphenyl-

11:12-benzofluoranthene (LXIV, p. 41).

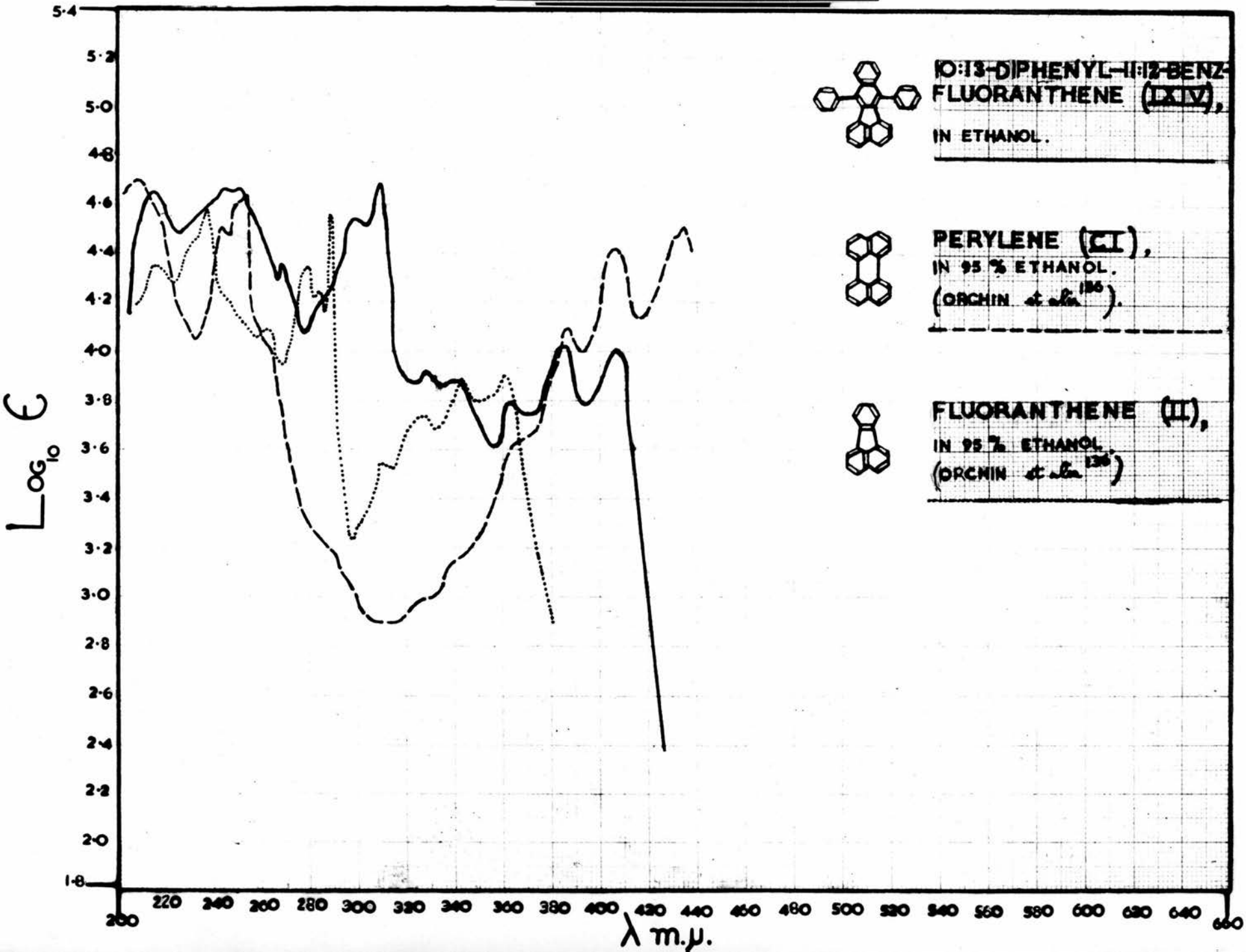
This strong evidence that A is an 11:12-benzfluoranthene derivative raises the question of its formation, and a probable answer appears in Scheme F:-



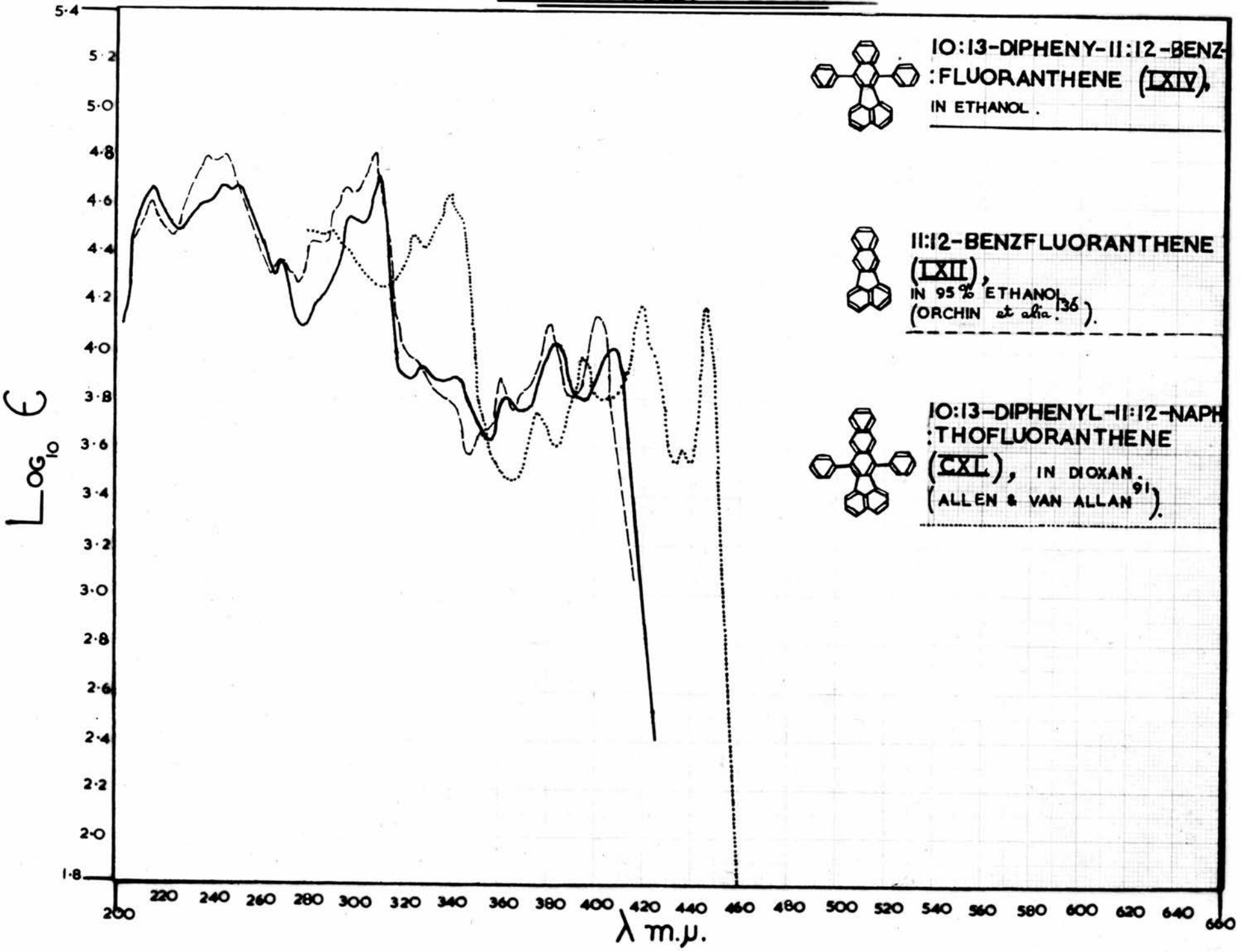
Scheme F

According to this Scheme the 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) produced initially ring-closes spontaneously at the temperature of the reaction by splitting off hydrogen to form 10:13-diphenyl-11:12-benzfluoranthene (LXIV). It is known that the hydrogen "x" in XXXII must be very active as it is attached to a butadiene system activated by three phenyl groups and a

ULTRA-VIOLET SPECTRA



ULTRA-VIOLET SPECTRA



10:13-DIPHENY-11:12-BENZ-
:FLUORANTHENE (LXIV),
IN ETHANOL.

11:12-BENZFLUORANTHENE
(LXII),
IN 95% ETHANOL
(ORCHIN *et alia*.[136]).

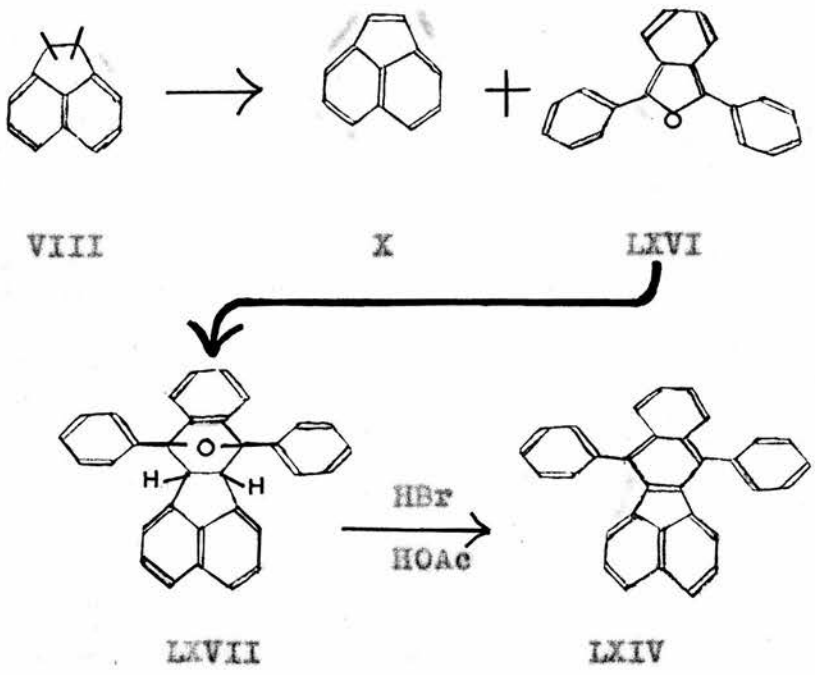
10:13-DIPHENYL-11:12-NAPH
:THOFLUORANTHENE
(CXL), IN DIOXAN.
(ALLEN & VAN ALLAN[91]).

naphthalene group (a benzene nucleus being roughly equivalent to a double-bond in conjugating power[92]), moreover, a study of a model of XXXII shows that the hydrogen "x" lies very close to the phenyl group "y". It is, therefore, not unlikely that a ring-closure of the type suggested occurs.

The dehydrogenation of LXIII must be assumed to occur instantaneously under the conditions of the reaction, as no compound corresponding to LXIII was ever isolated, and the diphenylketene may aid this. As the reaction was carried out under a stream of nitrogen no evolution of CO_2 or of hydrogen could be seen.

The evidence for the above series of reactions, namely the apparent structure of compound A, as suggested by its analysis and ultra-violet spectrum, and the fact that it does not hydrogenate, are by no means conclusive. 10:13-Diphenyl-11:12-benzfluoranthene (LXIV) has, however, been synthesised by Bergmann[141] by refluxing acenaphthylene (X) with diphenylisobenzfurane[263] (LXVI) to give the adduct LXVII which was converted into LXIV. A specimen of this substance was kindly supplied by Professor Bergmann and showed no depression in the melting-point when mixed with compound A. Compound A is therefore 10:13-diphenyl-11:12-benzfluoranthene (LXIV).

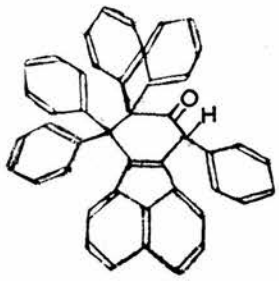
The proof of the identity of compound A does not prove that the hypothetical series of reactions for its formation (Scheme F, p. 39) is correct, but it seems very probable, and further evidence

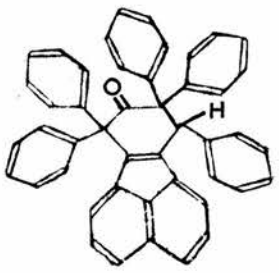


suggesting the existence of the intermediate XXXII, which probably caused the red colour noted whilst eluting the crude product from the column, will be discussed at a later stage (p.55).

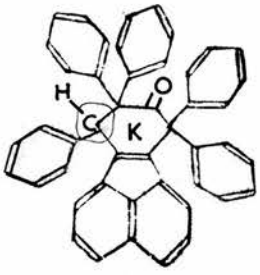
Compound B. This compound was shown by analysis to contain oxygen and to have a high molecular weight, and it seemed likely from the analysis that it was either compound XLVII or XLVIII.

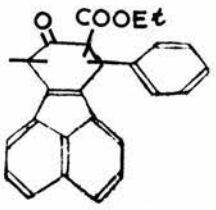
Compound B formed lemon yellow prisms with a sugary appearance, their colour being very similar to that given by the acenaphthylene chromophore, and the spectrum of the compound (p. 45) is very similar to that of 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one which is discussed later in this Thesis (p.123). Both spectra show peaks between 320 m.μ. and 345 m.μ. and have the same general shape as the spectrum of acenaphthylene (X, p. 45). Thus there is strong evidence that





XLVII XLVIII

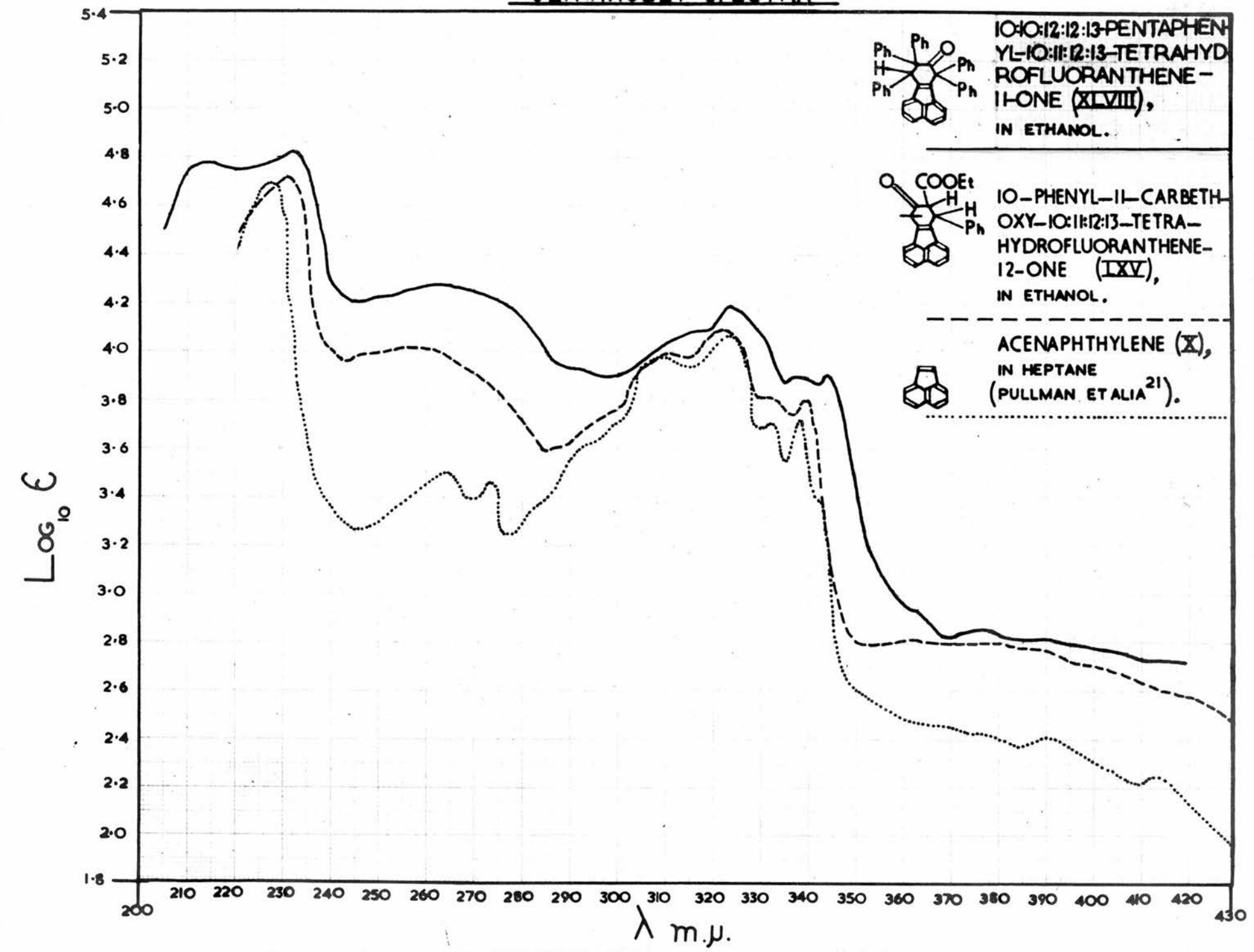




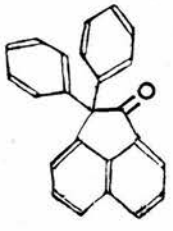
X XLVIII LXV

compound B has an acenaphthylene (X) nucleus, and is either XLVII or XLVIII. Preparation of models of XLVII and XLVIII shows that XLVIII is the more likely to be formed because it lacks the overcrowding caused by the phenyl substituents in the 10 and 11 positions in XLVII, and hence the likelihood is that compound B is XLVIII, namely, 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one. Compound B is thus both an olefine and a ketone, and attempts were made to hydrogenate the compound (at room temperature), and to prepare a hydrazone and a 2:4-dinitrophenylhydrazone. None of these attempts was successful, but, in view of the highly substituted nature of the "K" ring, this is not entirely surprising. In the case of the failure to hydrogenate, apart from the mechanical protection given to the double bond by the bulky substituents to the "K" ring, the electrophilic

ULTRAVIOLET SPECTRA

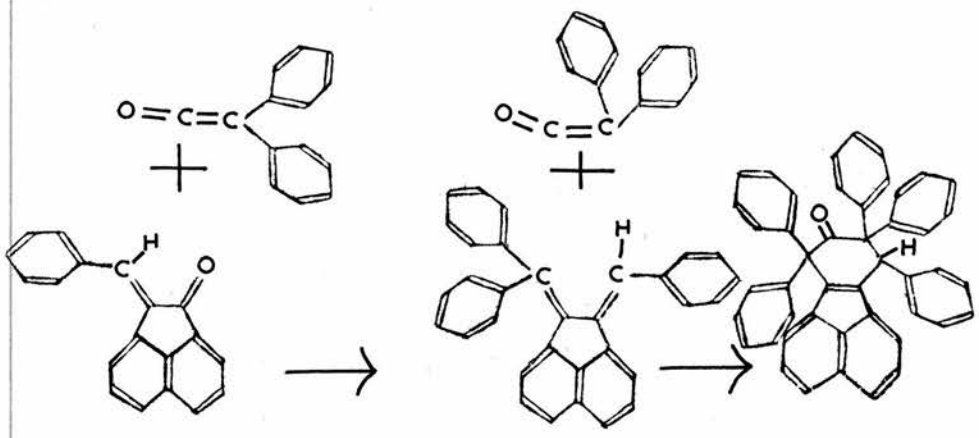


nature of the five phenyl substituents and the ketonic and peri-naphthylene substituents would be expected to render the acenaphthylenic double bond in XLVIII highly inactive.[92,99] The inability of the 11 carbonyl group to form a hydrazone or a 2:4-dinitrophenylhydrazone is explicable on the same grounds, especially in this case as the bulky phenyl substituents will effectively prevent the approach of a large molecule like 2:4-dinitrophenylhydrazine or even a smaller molecule like hydrazine. Similar examples of this behaviour are known, as for instance, 7:7-diphenylacenaphthene-8-one (CCXXIII), is not recorded as yielding normal ketonic derivatives.[265,264]



CCXXIII

In order to obtain some further evidence of the structure of compound B, the mode of formation of the compound was considered. It was postulated that excess diphenylketene (XLII) reacted with the active 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) as soon as it was produced in the reaction, to form XLVIII by a simple diene reaction.

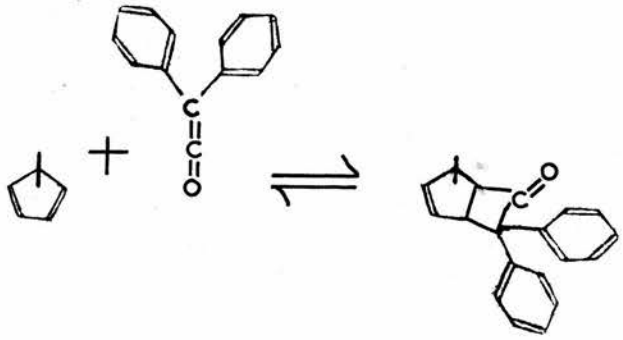


IV XLII XXXII XLVIII

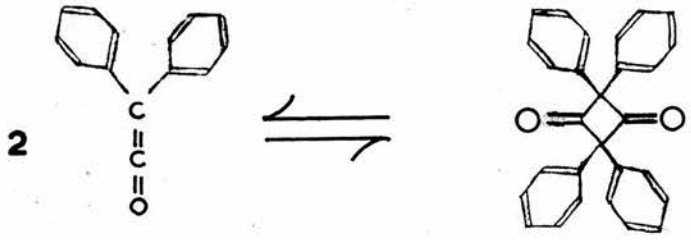
The addition of diphenylketene (XLII) to double bonds is well known, and examples from the literature are the formation of an adduct LXXII with cyclopentadiene (LXXI)[195], the formation with quinoline (LXXIII) of a diphenylketene - quinoline complex (LXXIV)[125,132,178], and the polymerisation of diphenylketene to form 2:2:4:4-tetraphenylcyclobutane-1:3-dione (XLIX, p. 82)[125].

Such additions by ketenes are in many cases reversible[125,(178),196], as are the above examples, and this suggested the possibility that the formation of XLVIII might also be reversible. Identification of the break down products of compound B would effectively confirm the composition of that molecule.

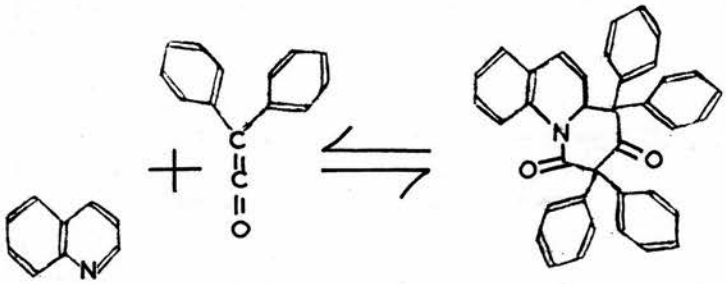
A quantity of compound B was therefore boiled under reflux for several hours in α-methylnaphthalene (B.P. 243°C.) to try the effect of heating the substance at a high temperature. Very quickly, a brilliant blue fluorescence developed, and on crystallisation, a few milligrammes of a yellow crystalline product were obtained, which was proved by mixed melting-point to be 10:13-diphenyl-11:12-benzfluoranthene (LXIV).



LXXI XLII LXXII

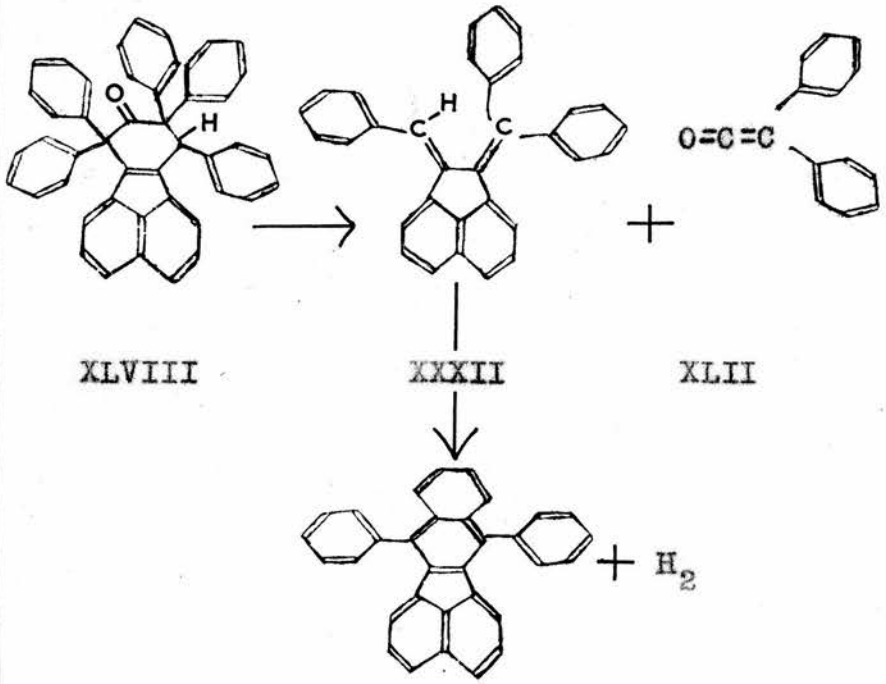


XLII XLIX



LXXIII XLII LXXIV

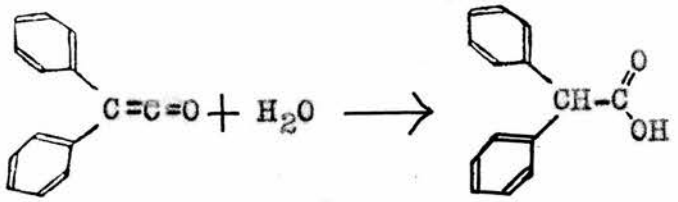
It seemed likely that this last product was formed by the reaction shown below (c.p. Cook and Hewett).[104] The temperature of the reaction was fairly high, and, in view of the known ease of formation of LXIV, it seemed probable that the postulated ring-closure would occur. The next stage, therefore, was to produce evidence of



XLVIII XXXII XLII

LXIV

diphenylketene (XLII) having been formed. Refluxing of larger quantities of compound B in α-methylnaphthalene yielded a few milligrammes of diphenylacetic acid (LXXVI), but attempts to prove the presence of diphenylketene (XLII) by the addition of aniline, with which the ketene forms a characteristic derivative,[127,143,157] were unsuccessful. The presence of diphenylacetic acid (LXXVI), however, was good evidence of the formation of diphenylketene (XLII), as the slightest trace of water would rapidly convert XLII into the acid LXXVI.



XLII LXXVI

Confirmation of this was obtained by treating compound B with sodium ethoxide and potassium hydroxide solutions at the temperature of the water bath. In both cases the presence of diphenylacetic acid (LXXVI) was proved among the decomposition products, and in both cases a deep crimson solution with a strong blue fluorescence was produced, suggesting that the intermediate 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) was not being immediately ring-closed to form LXIV at this temperature. The evidence for the existence of XXXII is discussed at a later stage (p. 55).

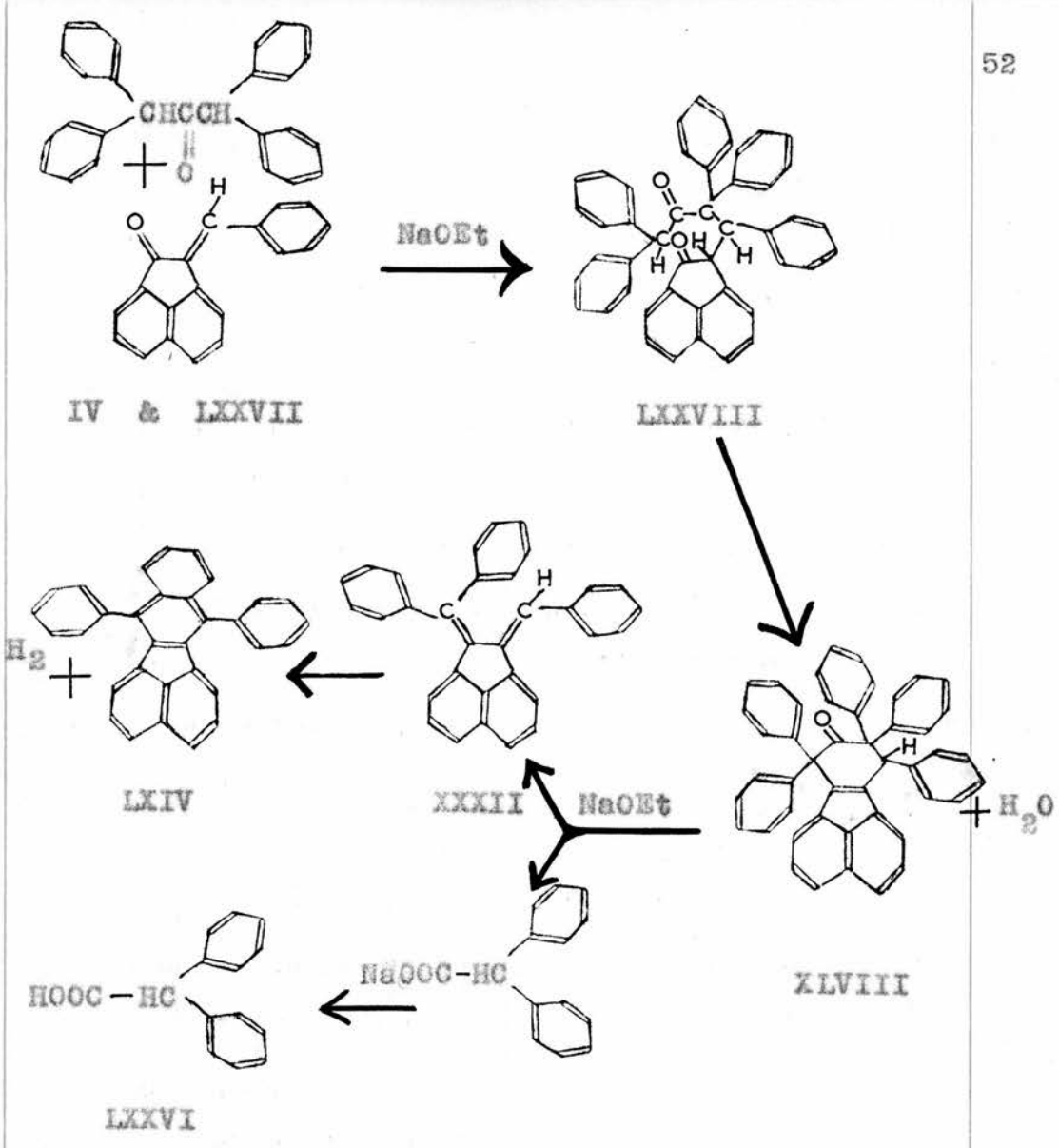
A direct proof of the formation of diphenylketene (XLII) on heating compound B was provided by heating 0·1 gm. of the substance under high vacuum in a very simple microdistillation apparatus (Fig.I, p. 181). The compound B was quickly heated to about 250°C. in high vacuum and the gases distilling over were collected in a bulb cooled in solid CO_2 and containing a little aniline. Long needle shaped crystals grew within a few minutes, and were identified as diphenylacetanilide by mixed melting-point with a known sample of diphenylacetanilide, thereby proving that diphenylketene had been formed.[127,143,157]

Now that the components of a compound B, diphenylketene (XLII) and 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII), had been identified, it only remained to verify how the components were joined together to prove the structure of the compound.

In Part II of this Thesis, Michael type con-

densations carried out with 7-benzylideneacenaphthene-8-one (IV) are discussed, and a reaction of this type, in which sym-tetraphenylacetone (LXXVII) was condensed with IV, and which would be expected to yield XLVIII (Scheme G), was therefore tried as it might provide additional evidence of the structure of compound B. The reaction requires an alkaline catalyst, and therefore any XLVIII formed would be decomposed as described above (p. 50) and evidence of its formation would have to be obtained by isolation of its known decomposition products. Refluxing the reactants with sodium ethoxide (see p. 141) gave a deep red solution, and on working up both diphenylacetic acid (LXXVI) and 10:13-diphenyl-11:12-benzfluoranthene (LXIV) were isolated and identified, thus providing a second synthesis for LXIV and confirming the structure of compound B as XLVIII (see also p. 61). It should be noted that LXXVIII, the only completely unknown compound in the synthesis shown in Scheme G, would be expected to ring - close automatically, as do simpler compounds of the same type (p. 109).

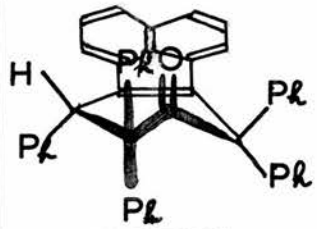
This synthesis, combined with our knowledge of the decomposition products of compound B, and the improbability of XLVII being formed (p. 44), provides very strong evidence that compound B is 10:10 :12:12-:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII).



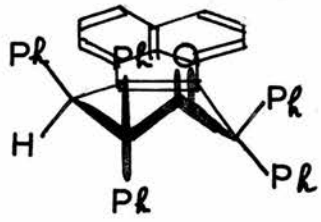
Scheme G.

Study of a model of XLVIII shows that the volume of the five phenyl, one peri-naphthylene, one ketonic, and one hydrogen groupings attached to the cyclohexene ring "K" is so large that rotation of the phenyls is likely to be prevented, and they are packed so closely together round the cyclohexene ring that it in turn is likely to be distorted by the close packing of its substituents. The interchange which would be expected between forms XLVIIIA and XLVIIIC and forms XLVIIIB and XLVIIID may, therefore be difficult, as the planar form through which the molecule passes when changing

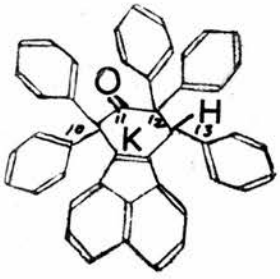
would cause impingement of the substituent atoms one upon another (c.p. Sachse-Mohr theory of strainless rings). Thus, an asymmetric centre may be produced by the actual shape of the molecule XLVIII, and this, combined with the asymmetric carbon atom in the 13 position, would lead to the possibility of the formation of diastereoisomerides as well as optical isomerides, as is shown below.



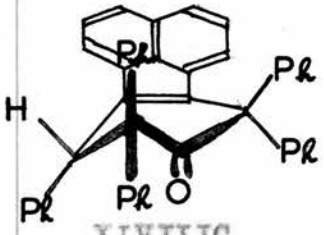
XLVIIIA



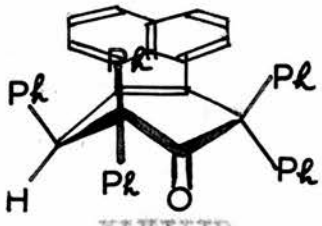
XLVIIIB



XLVIII



XLVIIIC



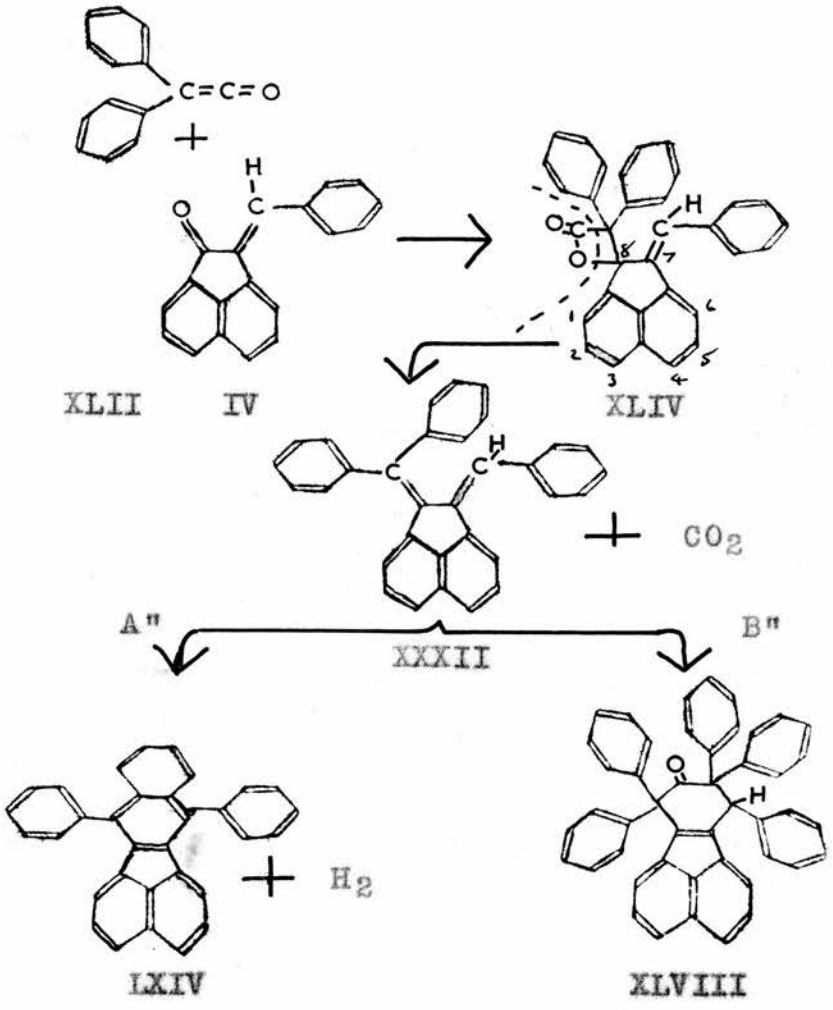
XLVIIID

Compound C. Only a few mg. of compound C were obtained, but the analysis of the compound and its melting-point at 174-6°C. accord closely with Staudinger's data for a polymer of diphenylketene, M.P. 176°C., obtained by heating the latter, but of which he did not determine the structure.[260]

Compound D. This compound formed fine, deep orange red needles subliming above 290°C., and melting at 296-302°C. Insufficient of the compound was obtained for analysis, and nothing is known of its structure, except that the high melting-point

suggested that the molecule was large.

From the evidence submitted above, diphenylketene (XLII) and 7-benzylideneacenaphthene-8-one (IV) interact according to Scheme H.



Scheme H

As the reactions A" and B" occur together, variation in the proportions of the reactants and the conditions of the reaction should result in a variation in the proportion of the products A and B. Accordingly, additions of different proportions of diphenylketene and 7-benzylideneacenaphthene-8-one were carried out, and the products separated. It was found that with one mole of the ketene and one mole of IV, compound A could be isolated but no compound B, while with four moles of the ketene and

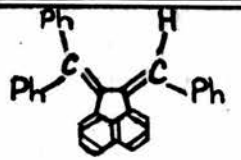
one mole of IV, under similar reaction conditions, the products were compound B (64%) and compound A (3%), thus supporting the postulated parallel reactions A" and B" shown in Scheme H.

The formation of 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) has already been mentioned, and some evidence of the existence of this compound and its precursor the β-lactone XLIV might be expected. In fact, no direct evidence of the existence of the β-lactone was found, but as one of the carbon atoms of the β-lactone ring, which is inevitably highly strained, is also in the distorted five membered ring of the acenaphthene nucleus, the ephemeral existence of this compound is not surprising.

The existence of compound XXXII explains the formation of both LXIV and XLVIII, and explains the conversion of XLVIII into LXIV by the action of heat or alkali, and though compound XXXII could not be isolated in the solid state, evidence of its existence was found.

It has already been mentioned (p. 50) that compound XLVIII, when treated with alkali, immediately gives a crimson coloured solution with a brilliant purple fluorescence in ultra-violet light.[93,94,95,96] Maxim claimed that all his diarylidene - and dialkylidene-acenaphthenes were strongly coloured compounds, presumably because of the chromogene CVII, and it was therefore thought likely that the red colour was caused by the presence of trans-7-benzylidene-8-diphenylmethyleneacenapthene

ULTRA-VIOLET SPECTRA



7-BENZYLIDENE-8-DIPHENYLMETHYLENEACENAPHTHENE (XXXII), QUALITATIVE IN CYCLOHEXANE.

UNCHROMATOGRAPHED XXXII, QUALITATIVE IN CHLOROFORM CONTAINING 0·2 % ETHANOL (P. 59).

ACENAPHTHYLENE (X), (CRAIG et al.[185])

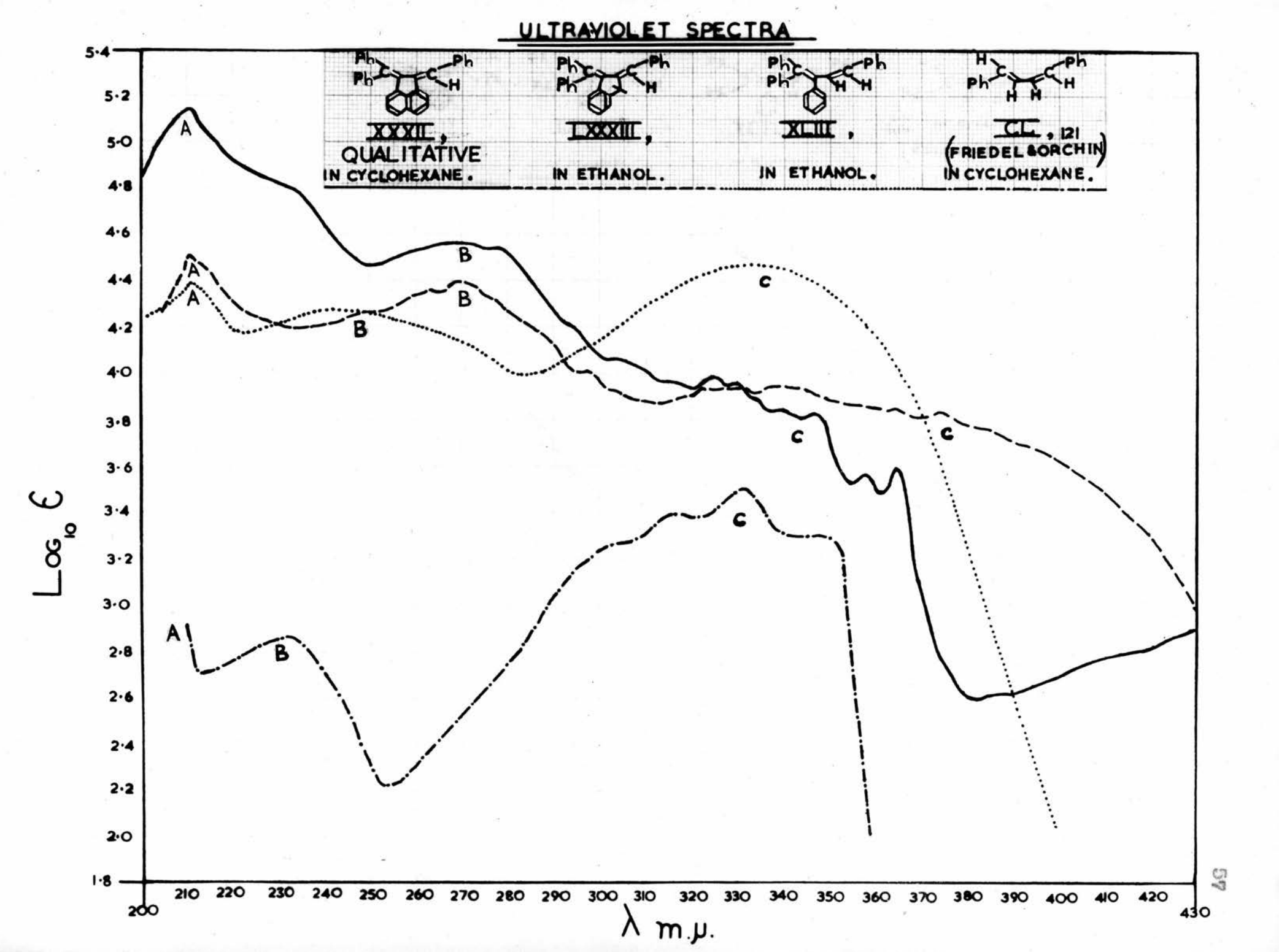
$\text{Log}_{10}\,\epsilon$

5·4 5·2 5·0 4·8 4·6 4·4 4·2 4·0 3·8 3·6 3·4 3·2 3·0 2·8 2·6 2·4 2·2 2·0 1·8

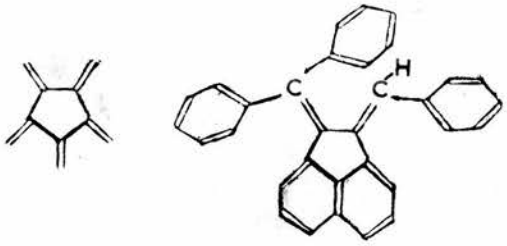
200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620 640 660

λ m.μ.

ULTRAVIOLET SPECTRA



(XXXII), and attempts were made to isolate this



CVII

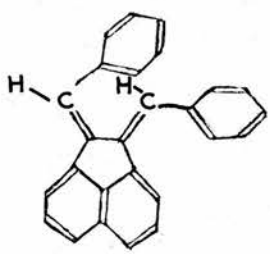
XXXII

compound. The compound was prepared by the action of alkali on solutions of XLVIII and attempts were made to crystallise the red solutions which were formed. No crystalline solid was obtained, and the red compound was therefore purified by chromatography on alumina, and isolated in solution by selective elution with petrol, and its ultra-violet spectrum observed in cyclohexane.

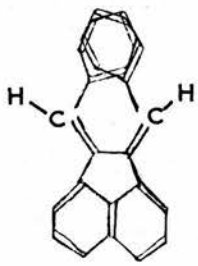
The qualitative ultra-violet spectrum of the red compound in cyclohexane suggests that it was a pure compound, and the profile of the curve between 350 mμ. and 380 mμ. is similar in shape to the corresponding part of the ultra-violet spectra of many compounds that contain an acenaphthylenic or naphthalenic nucleus (see spectra p. 5 and also p. 56). The general shape of this spectrum resembles the shapes of the spectra of the other substituted butadienes shown in the family of curves on p. 57, in that each has three distinct humps, and there is a distinct gradation of shape as the complexity of the substituents increases. The spectrum of XXXII substantially resembles that of the compound believed to be 3-diphenylmethylene-

2-benzylidenehydrindene (LXXXIII, p. 75). The spectrum in chloroform of an unchromatographed specimen of the red compound (p. 56) suggests that this contained some 10:13-diphenyl-11:12-benzfluoranthene (LXIV) as impurity, as the peaks at 387 mμ. and 410 mμ. correspond with those of LXIV at 384 mμ. and 407 mμ. and considered together, the above spectroscopic evidence substantially supports the presumption that the red compound is 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII).

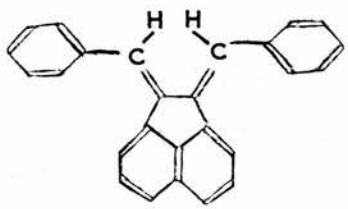
Other red compounds derived from ketenes are known[146,167,260] and might conceivably be related to the red compound prepared in this work, but it is unlikely that this compound is related to the red compounds obtained with ketenes and described later in this Thesis (p. 96), as these would not elute from alumina with petrol.



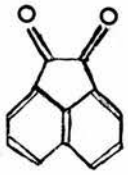
LVI



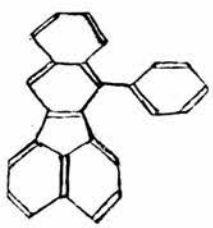
LVII



LVIII (V)



L



LIX

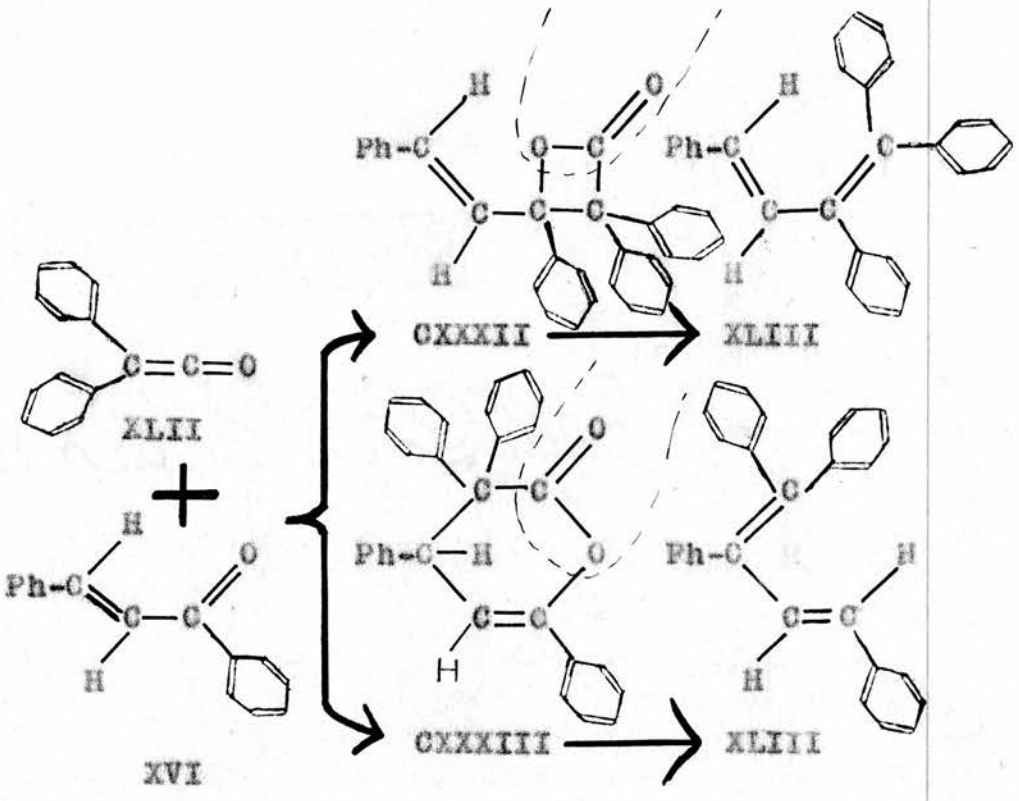
Some of the conclusions reached concerning 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) would seem likely to apply to J. Stafford's work at Cambridge on 7:8-dibenzylideneacenaphthene (V).[103] The Cambridge worker isolated three hydrocarbons (see ps. 33—35) from his syntheses, which he believed were isomeric, and on the basis of their analyses, their infra-red spectra, and a comparison of their physical properties with those of the geometric isomers of distyryl,[133] he suggested that all three compounds were probably geometric isomers of 7:8-dibenzylideneacenaphthene, LVI, LVII, LVIII, even though:

1. Two of these compounds could not be hydrogenated.
2. One of these compounds did not yield acenaphthenequinone (L) on ozonolysis (ozonolysis is not described with the others).
3. The cis-cis form LVII is shown by models to be unlikely to exist.
4. The so - called cis-cis form LVII and the so - called cis-trans form LVI were not transformed into the stable trans-trans form LVIII as might be expected from a comparison with distyryl.
5. The cis-trans form LVI might be expected, by comparison with XXXII, to ring - close to yield 10-phenyl-11:12-benzflouranthene (LIX), or a partly hydrogenated derivative of this.

In view of later knowledge, therefore, it might be suggested that compound A', of M.P. 163°C., which absorbed two moles of hydrogen, was a 7:8-dibenzylideneacenaphthene, probably the relatively stable trans-trans form LVIII, and it is noteworthy that this compound was fluorescent, a property shown by the presumably trans-trans form of 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) and by the trans-trans form of distyryl[133] (p. 34). Compound B', of M.P. 242°C., may have been 10-phenyl-11:12-benzfluoranthene (LIX) or a partly hydrogenated derivative of this formed by a ring-closure of LVI. Compound C', of M.P. 327°C., which did not hydrogenate or yield acenaphthenequinone (L) on ozonolysis, would seem from its high melting-point most likely to have been a polymer or other complex derivative. This is confirmed by the molecular weight of approximately 478 reported for this compound. (Theory for V is 330·4).

So far in this section, the argument has been based on the assumption that diphenylketene (XLII) reacts with 7-benzylideneacenaphthene-8-one (IV) as if it was a saturated ketone, such as fluorenone[179] (XXIX) or benzophenone[181,180] (CXXX), with which the ketene would be expected to form initially a β-lactone (such as XLIV in Scheme H, p. 54). This, however, is not the only possibility, and it has been shown by Staudinger and Endle[144,126,145] that α:β-unsaturated ketones such as chalkone (XVI) initially form unsaturated δ-lactone adducts, such as CXXXIII, with diphen-

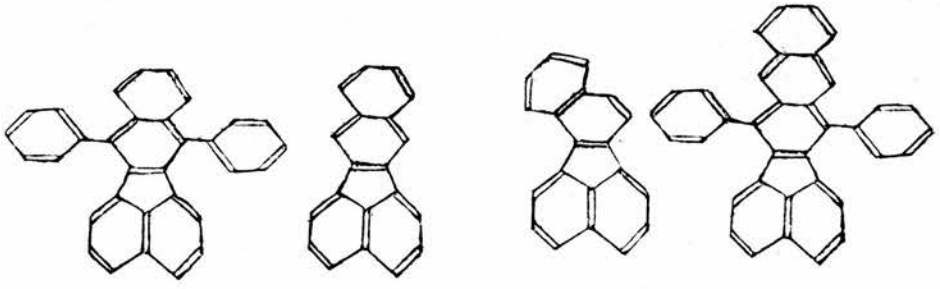
ylketene (XLII), in place of the expected β-lactone adduct (e.g. CXXXII, in Scheme J). This is in accordance with Thiele's theory of partial valency for conjugated compounds. It should be



Scheme J

noted that in Scheme J, with chalkone (XVI) as starting material, the final reaction product after the removal of CO_2, is the same for both the β-lactone and δ-lactone intermediates, namely 1:3:4:4-tetraphenylbutadiene (XLIII). In the reaction between 7-benzylideneacenaphthene-8-one (IV) and diphenylketene (XLII), however, this would not be the case, and an entirely different set of products would be obtained. Schemes K and L compare the compounds XLIV, XXXII, LXIV and XLVIII postulated as

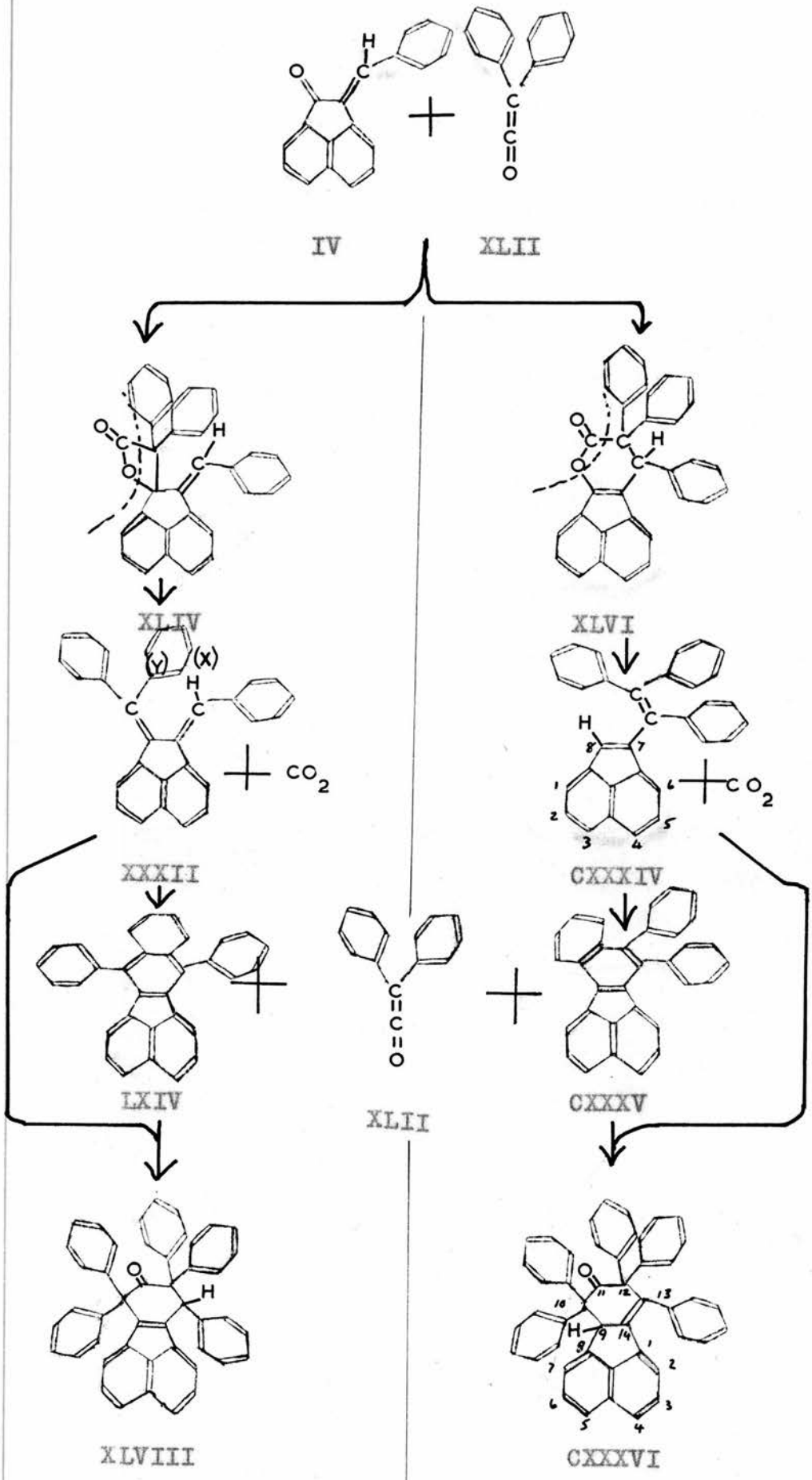
being produced from the β-lactone with the possible alternatives were the initial adduct a δ-lactone. Although the alternative compounds suggested in Scheme L are isomeric with the corresponding compounds in Scheme K, and therefore have the same composition, they are theoretically unlikely to be formed, principally because of the free rotation about the 7:8 bond in 7-acenaphthylenetriphenylethylene (CXXXIV). It was postulated that XXXII ring-closed to form LXIV because the rigid bond system of XXXII forced the "y" ring into close proximity with the "x" hydrogen atom, thus enabling the reaction to occur, but if free rotation exists at the 7:8 bond of the acenaphthylene part of the molecule as in CXXXIV (as well as in the phenyl which can rotate freely in both cases), ring-closure to form compound CXXXV would seem much less likely. As a mixed melting-point between the product believed to be LXIV and a specimen of LXIV prepared by Bergmann[141] by an unambiguous synthesis (see p.43) showed no depression, this is placed beyond doubt.



LXIV LXII CIV CXL

The ultra-violet spectrum of LXIV is compared on p. 66 with those of 10:11-benzfluoranthene (CIV), and 11:12-benzfluoranthene (LXII), as observed by Orchin et alia.[32,136] These workers did not distinguish the above compounds, but the significant difference between the spectrum of their low melting-point compound, and the spectra of their high melting-point compound, LXIV and CXL (p. 41) confirms that the low melting-point compound was 10:11-benzfluoranthene (CIV) and the high melting-point compound 11:12-benzfluoranthene (LXII),[137,138] while at the same time confirming the identity of LXIV.

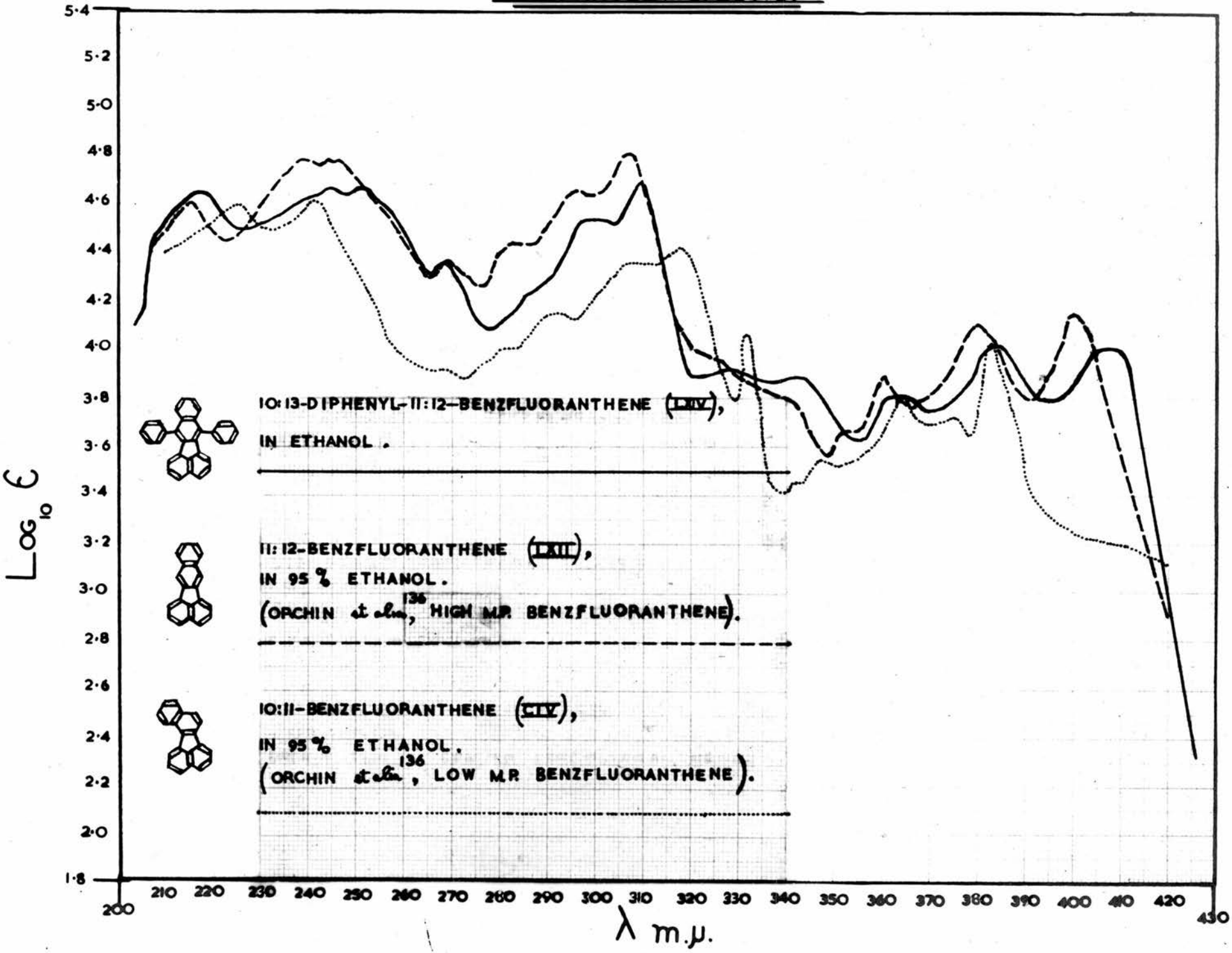
Theoretical considerations also suggest that 10:10:12:12:13-pentaphenyl-9:10:11:12-tetrahydrofluoranthene-11-one (CXXXVI) or 10:10:11:11:13-pentaphenyl-9:10:11:12-tetrahydrofluoranthene-12-one are not formed. The compound believed to be XLVIII was found to decompose on heating, or in the presence of alkali, to form LXIV. This may occur in the case of XLVIII by a simple reversal of the diene reaction by which it was formed, but in the case of CXXXVI it would be necessary for the hydrogen in the 9 position to migrate to the 13 position before XXXII and hence LXIV could be formed, otherwise, by simple reversal of the formative reaction, CXXXIV would be produced, which could not yield LXIV. Furthermore, CXXXVI would be expected to be a pale yellow compound, not showing the characteristic ultra-violet spectrum of an acenaphthylene derivative, but the compound believed to be XLVIII showed the brilliant yellow



Scheme K

Scheme L

ULTRAVIOLET SPECTRA

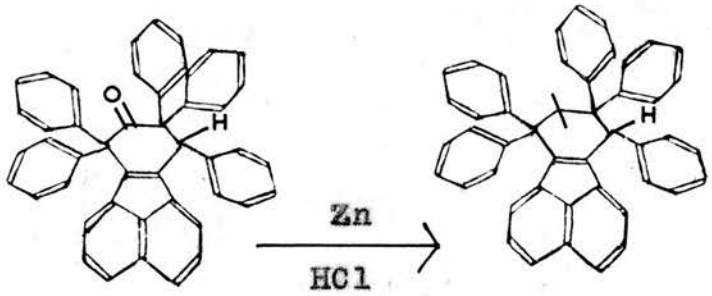


colour and the characteristic spectrum of an acenaphthylenic derivative (ps. 45, 69).

It seems certain, therefore, that this series of reactions is initiated by the formation of a β- and not a δ-lactone, and the weight of evidence in favour of the series of reactions shown in Scheme K, and for the individual compounds involved, would seem to place beyond reasonable doubt the rectitude of this Scheme as an explanation of the interactions of diphenylketene and 7-benzylidene-acenaphthene-8-one.

Before passing on to discuss the action of diphenylketene on 2-benzylidenehydrindene-3-one, a few other reactions attempted with LXIV and XLVIII will be mentioned.

The first of these reactions was the attempted Clemmensen reduction[158,159,160] of XLVIII to form the hydrocarbon 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene (LXXIX).

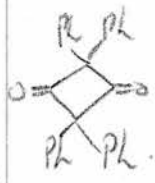


XLVIII LXXIX

No hydrocarbon LXXIX was obtained from these reductions, confirming the abnormal character of the ketonic grouping in XLVIII, but after prolonged refluxing, a few milligrammes of two products were

isolated, and the analyses of these indicated that they were formed by decomposition of the original molecule.

The first of these compounds was isolated as colourless needles of M.P. 245-6°C. which were shown by their ultra-violet spectrum (p. 85), analysis and mixed melting-point to be identical with a compound isolated from another diphenylketene (XLII) reaction (p. 82), and believed to be 2:2:4:4-tetraphenylcyclobutane-1:3-dione (XLIX).



The isolation of this compound (XLIX) suggested that the 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII) had been decomposed at the temperature of the reaction into diphenylketene (XLII) and presumably 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII), of which the second product isolated must be a derivative.

The second compound formed lemon yellow crystals of M.P. 192-4°C., the colour and ultra-violet spectrum of which strongly suggested that the substance was an acenaphthylene (X) derivative. The spectrum of the compound of M.P. 192-4°C. is shown on p. 69, along with the similar spectra of acenaphthylene[21] (X) and 7-(w-methoxybenzyl)-8-chloroacenaphthylene (LXIX, p.147).

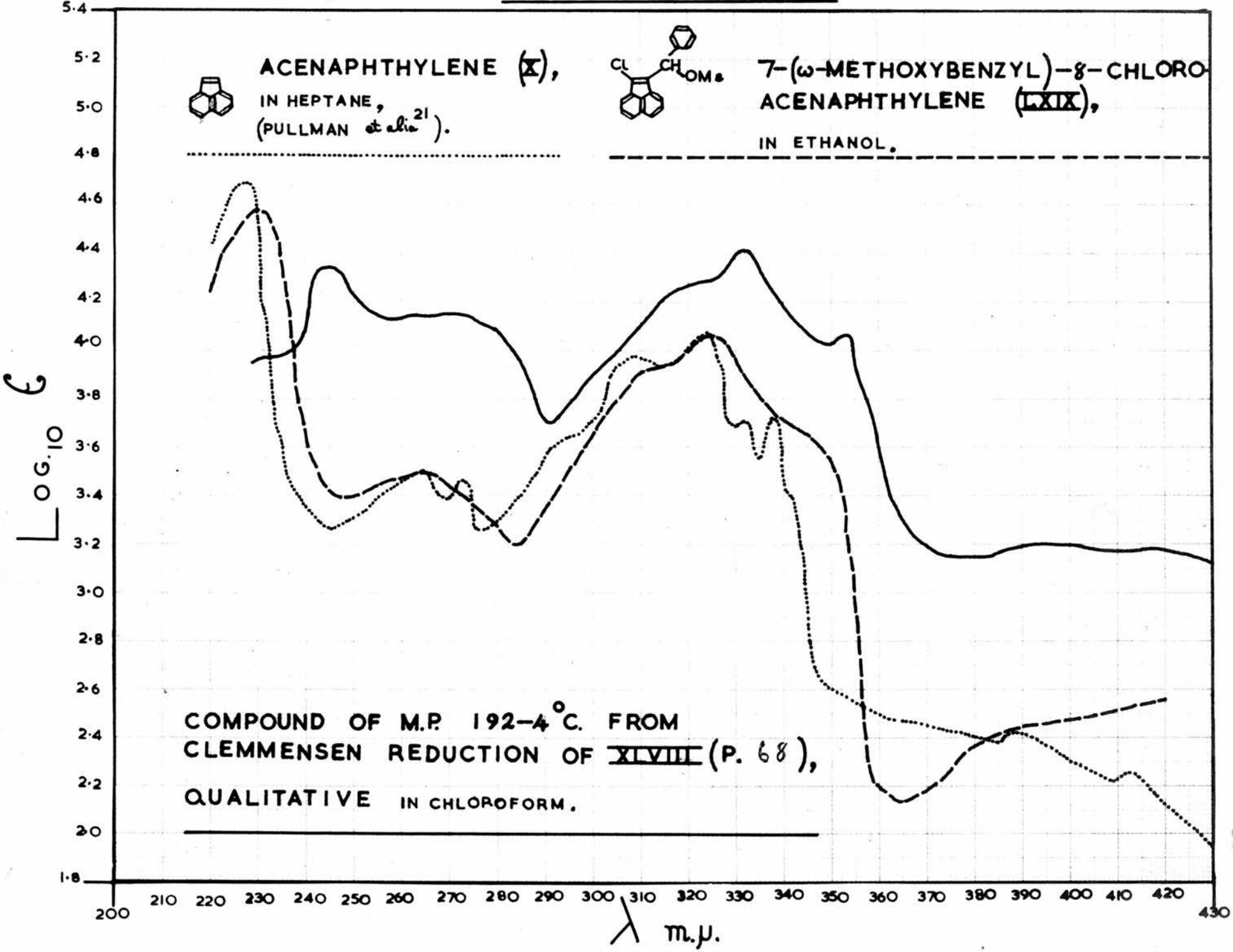
The second of these attempted reactions was an attempt to decompose 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII) by the action of radioactive energy from a 100 Curie cobalt^{60} source, in the hope that the quanta of

ULTRA-VIOLET SPECTRA

ACENAPHTHYLENE (X),
IN HEPTANE,
(PULLMAN *et alia*[21]).

7-(ω-METHOXYBENZYL)-8-CHLORO-ACENAPHTHYLENE (LXIX),
IN ETHANOL.

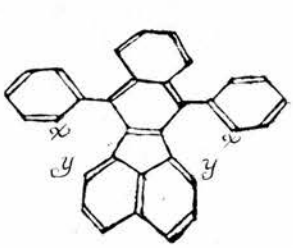
COMPOUND OF M.P. 192–4°C. FROM CLEMMENSEN REDUCTION OF XLVIII (P. 68),
QUALITATIVE IN CHLOROFORM.



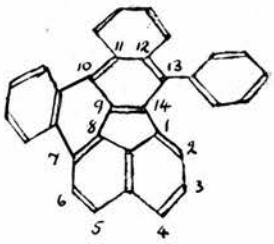
energy added to the cumbersome pentaphenyltetrahydrofluoranthenone by collision with the particles from the radioactive source might be sufficient to cause it to decompose, forming the highly fluorescent and therefore readily recognised 10:13-diphenyl-11:12-benzfluoranthene (LXIV).

A pure specimen of XLVIII was dissolved in pure benzene, chosen as solvent because of its low reactivity to radiation[147], two weighing bottles were filled to the brim with the solution, and one of them was placed near the source. The fluorescence of the exposed solution in ultra-violet light was compared from time to time with that of the control solution, and after two days there was a definite though slight blue fluorescence in the exposed solution. After a fortnight's exposure, the exposed solution was worked up, but the only solids that could be obtained were starting material and less than one milligramme of very thin colourless plates, M.P. 55°C., possibly of diphenyl (M.P. 70°C.) produced by the action of radioactive energy[147,268,269,273] on the solvent.

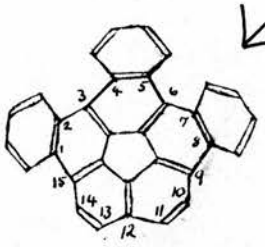
In the last of these attempted reactions, efforts were made to ring-close 10:13-diphenyl-11:12-benzfluoranthene (LXIV) by cyclodehydrogenation to form 13-phenyl-11:12-benz-7:10-naphthofluoranthene (LXXXV) or 1:2-4:5-7:8-tribenzcoronindene (LXXXVI).



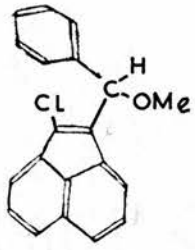
LXIV



LXXXV



LXXXVI

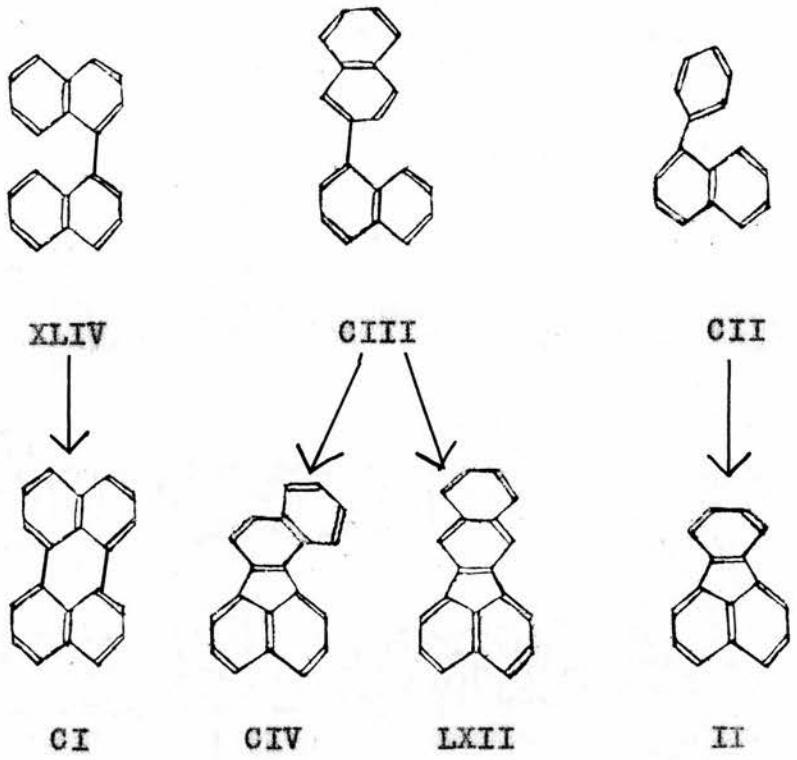


LXIX

X

Several examples of catalytic cyclodehydrogenations of aromatic compounds have been claimed by Orchin, Reggel, Friedel and Woolfolk.[136] For example, 1:1'-dinaphthyl vapour (XLIV) on treatment at 490°C. for two hours with a palladium on charcoal catalyst gave 11% of perylene (CI), 50% of the unchanged starting material being recovered.[136] Similarly, 1-phenylnaphthalene (CII), or its 2:3:4:5-tetrahydro derivative, when cyclodehydrogenated with a palladium on charcoal or a chromia catalyst yielded fluoranthene (II) up to 31% being obtained with the latter catalyst,[136] while 1:2'-dinaphthyl (CIII), when cyclodehydrogenated over chromia on alumina at 495-505°C. for 15 min., gave two compounds, believed from their analyses and ultra-violet spectra

to be 10:11-benzfluoranthene (CIV) and 11:12-benzfluoranthene, LXII, [136,137,138] (see p. 66).



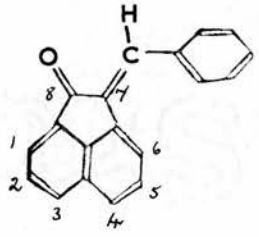
In view of the relative ease with which these vapour phase cyclisations occurred, and the good yields claimed, it would seem likely that 10:13-diphenyl-11:12-benzfluoranthene (LXIV) could be cyclised by dehydrogenation, especially as atoms 'x' and 'y' in LXIV are shown by models to be in very close proximity. This method would, therefore seem likely to provide a means of synthesising the substituted coronindene LXXXVI.

Attempts were made to cyclodehydrogenate LXIV using Adam's PtO_2 and palladium on charcoal catalysts in the liquid phase. Unchanged starting material was obtained from both reactions, and no other product could be isolated, though application of the more vigorous vapour phase cyclo-

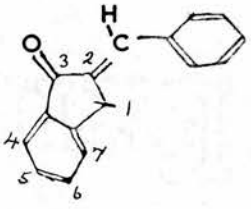
dehydrogenation methods of Friedel, Orchin, Reggel and Woolfolk might well produce a different result.

The Action of Diphenylketene on 2-Benzylidene-hydrindene-3-one

The interaction between 7-benzylideneacenaphthene-8-one (IV) and diphenylketene (XLII) suggested the possibility of a similar series of reactions between diphenylketene and other aromatic α:β-unsaturated ketones, such as 2-benzylidenehydrindene-3-one (LXXX).



IV



LXXX

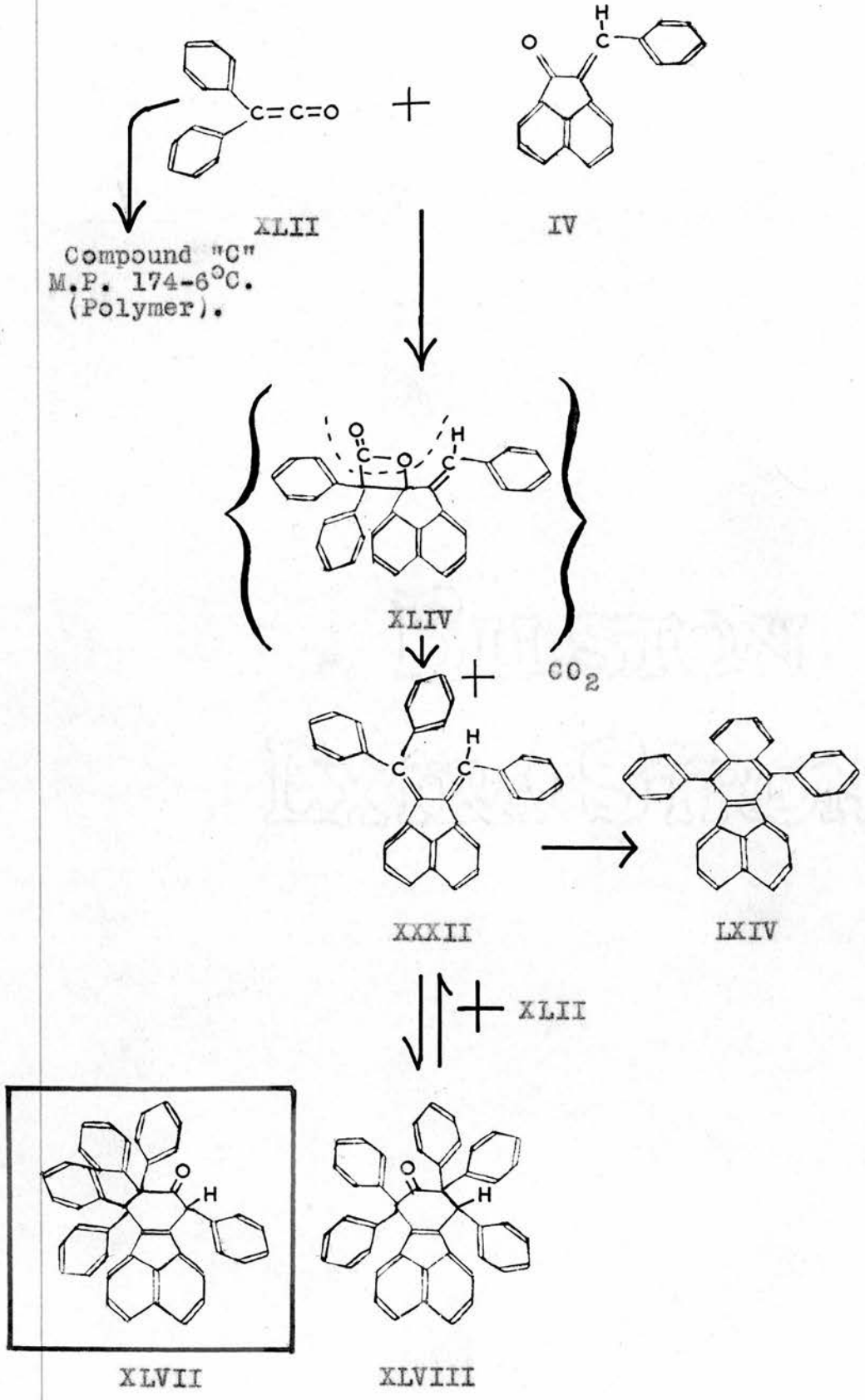
The series of reactions between diphenylketene (XLII) and 2-benzylidenehydrindene-3-one (LXXX) is analogous to the series of reactions discussed above (Scheme N) and is set out in Scheme M. The series of reactions is assumed to be initiated by the formation of a β-lactone, like the reactions in Scheme N, and the evidence for the existence of the compounds in Scheme M, and the reasons for the differences between the two Schemes are discussed in the following pages.

The interaction between diphenylketene[131] (XLII) and 2-benzylidenehydrindene-3-one[151-153] (LXXX) was carried out in a similar manner to the reaction with 7-benzylideneacenaphthene-8-one (IV), namely,

by heating the products together under nitrogen. Two reactions were carried out by heating LXXX (1 mol.) at 135 - 150°C. for 2½ hours with 1·0 and 1·3 mol. of the ketene XLII, respectively. Both reactions gave about a 50% yield of a colourless crystalline compound of M.P. 136·5-139°C. which formed a yellow melt, and gave yellow solutions. This compound is believed from analysis (see p. 191) to be 3-diphenylmethylene-2-benzylidenehydrindene (LXXXIII), and the only other product isolated from the above reactions was a few milligrammes of unidentified colourless crystals of M.P. 230-231·5°C.

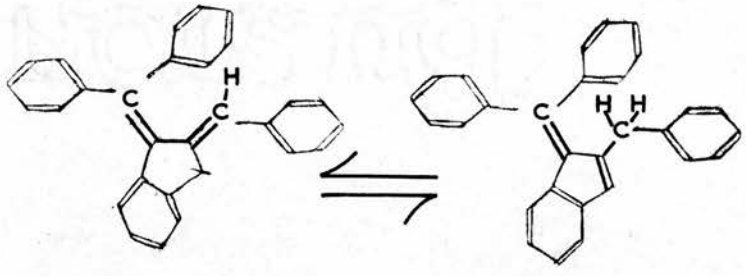
As with the reaction between diphenylketene (XLII) and 7-benzylideneacenaphthene-8-one (IV), by changing the reaction conditions, entirely different reaction products were obtained. In this case, 2-benzylidenehydrindene-3-one (LXXX, 1·0 gm.) was heated at 150-160°C. for four hours with four moles of diphenylketene (XLII), and gave rise to a high yield of a mixture of two products. These were separated by crystallisation from chloroform, and yielded in the one case colourless needles of M.P. 228-9°C., which analysis suggested might be 1:2:2:4:4-pentaphenyl-1:2:3:4-tetrahydrofluorene-3-one, LXXXIV, (or XCVI). The other product formed colourless prisms of melting-point 245-6°C., which analysis showed to have the same composition (and melting-point) as 2:2:4:4-tetraphenylcyclobutane-1:3-dione (XLIX), a dimer of diphenylketene (p. 82). The theoretical and experimental analyses of these compounds are shown in Table II (p. 83).

See overleaf.

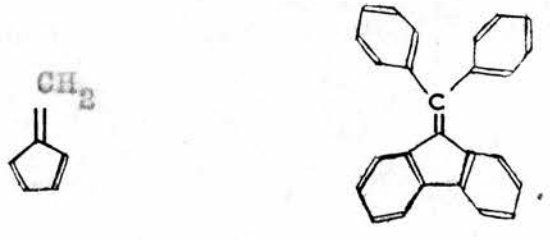

XLII
IV
Compound "C"
M.P. 174-6°C.
(Polymer).
XLIV
CO_2
XXXII
LXIV
XLII
XLVII
XLVIII

Scheme N

The compound of M.P. 136·5-139°C was soluble in ethanol giving a bright yellow solution, which did not fluoresce in ultra-violet light, and from which colourless crystals were obtained which gave a yellow melt. This change in colour, which appeared to be reversible, would suggest the possibility that the molecule exists in two tautomeric forms, one in solution and the other in the solid state, though it is noteworthy that 9-diphenylmethylenefluorene (XXII), which cannot tautomerise, is also yellow in solution, but not in the solid state. Theoretically it is possible that 3-diphenylmethylene-2-benzylidenehydrindene (LXXXIII) could tautomerise into 3-diphenylmethylene-2-benzylindene (LXXXVIII), and as this is a derivative



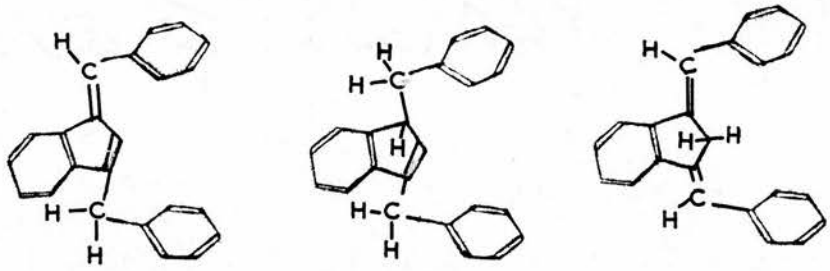
LXXXIII LXXXVIII



CXLII XXII

of fulvene (CXLII), which is yellow, it can at

least be postulated that the yellow compound in solution is the indene form LXXXVIII. Hydrogenation of this compound leads to the absorption of only one mole of hydrogen, just as the reduction of the similar fulvene derivative 3-benzyl-1-benzylideneindene (LXXXIX) with aluminium amalgam in wet ether leads to the reduction of only one double-bond, forming 1:3-dibenzylindene (LXXXVII),[154] though this is inconclusive as a distinction between the tautomers as both might add only one mole of hydrogen.

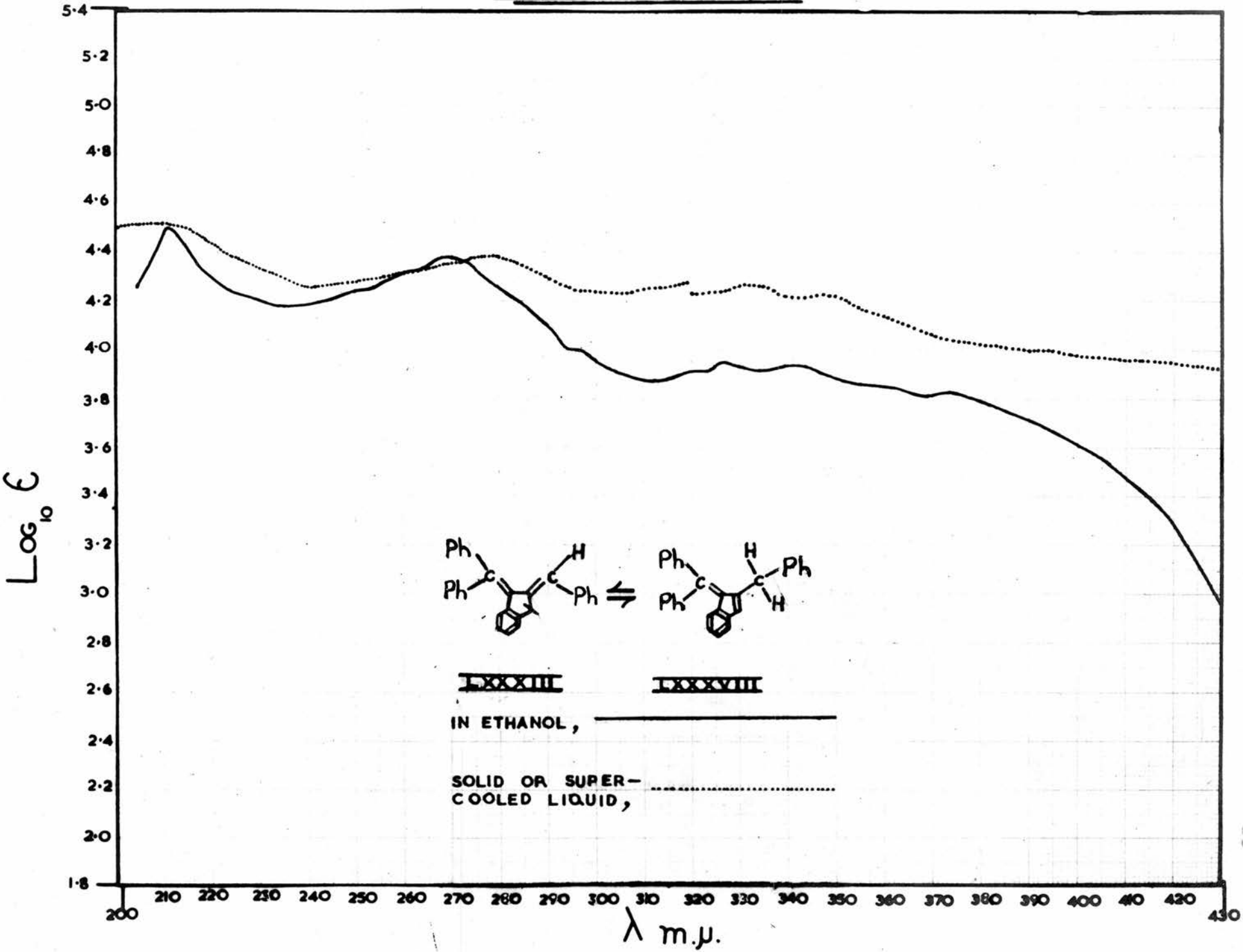


LXXXIX LXXXVII XC

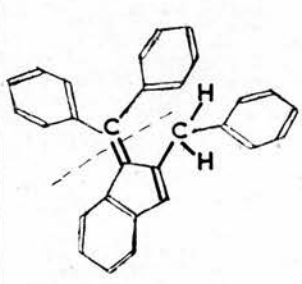
A similar isomerism may occur with 3-benzyl-1-benzylideneindene (LXXXIX) which is obtained from benzaldehyde and 1-benzylindene as yellow plates, M.P. 137-137·5°C.,[154] and from the reduction of 3-(w-chlorobenzyl)-1-benzylideneindene as a colourless monomeric compound of M.P. 212-3°C.,[154,155] isomeric with the yellow compound, and which yields the latter on heating. It might be suggested that the isomeric colourless substance is 1:3-dibenzylidenehydrindene (XC).

The ultra-violet spectrum of the product of M.P. 136·5-139°C. from the interaction of XLII and

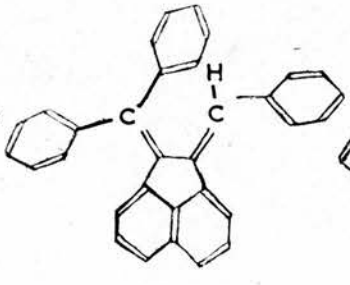
ULTRAVIOLET SPECTRA



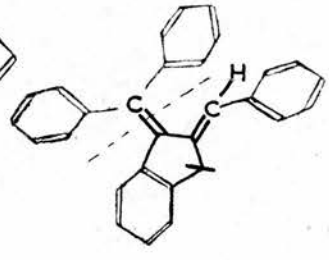
LXXX was observed in solution in ethanol, and also as a solid film, or more likely as a supercooled liquid film, formed by evaporation of the solution on the cell wall. The spectra are shown on p. 80, and the lack of clearly defined maxima and minima confirms that the substance was not a single compound. It is noteworthy that the maxima on the curve for the solution have nearly the same wavelengths as the maxima exhibited by the ultra-violet spectrum of the compound believed to be 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII, p. 57), and the spectrum resembles the spectra of the other butadienes shown on the same page in that each has three distinct humps, suggesting that the butadiene form LXXXIII does exist in the solution, presumably in equilibrium with the fulvene form LXXXVIII.



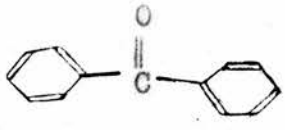
LXXXVIII



XXXII



LXXXIII



CXXX

The last piece of evidence in support of the identity of the compound of M.P. 136·5-139°C. was obtained by oxidation. Alone amongst the likely reaction products shown in Scheme M, both LXXXIII and LXXXVIII on chromic acid oxidation, would be expected to give inter alia benzophenone (CXXX). Chromic acid oxidation of 0·1 gm. of the compound in glacial acetic acid did in fact yield benzophenone (CXXX), which was isolated and identified as its 2:4-dinitrophenylhydrazone.

The synthesis, analysis, hydrogenation, oxidation, ultra-violet spectrum, and colour in the solid and liquid phases of the compound of M.P. 136·5-139°C. therefore suggest that it is 3-diphenylmethylene-2-benzylidenehydrindene (LXXXIII) or its tautomer LXXXVIII.

The second compound to be discussed is the product isolated from the reaction of LXXX with excess diphenylketene which melted at 245-6°C., and decomposed with the evolution of gas at about 300°C. This attribute, together with its analysis, suggested the compound to be 2:2:4:4-tetraphenylcyclobutane-1:3-dione (XLIX, lit. M.P. 244-5°C.), a dimer of diphenylketene (XLII).[260]

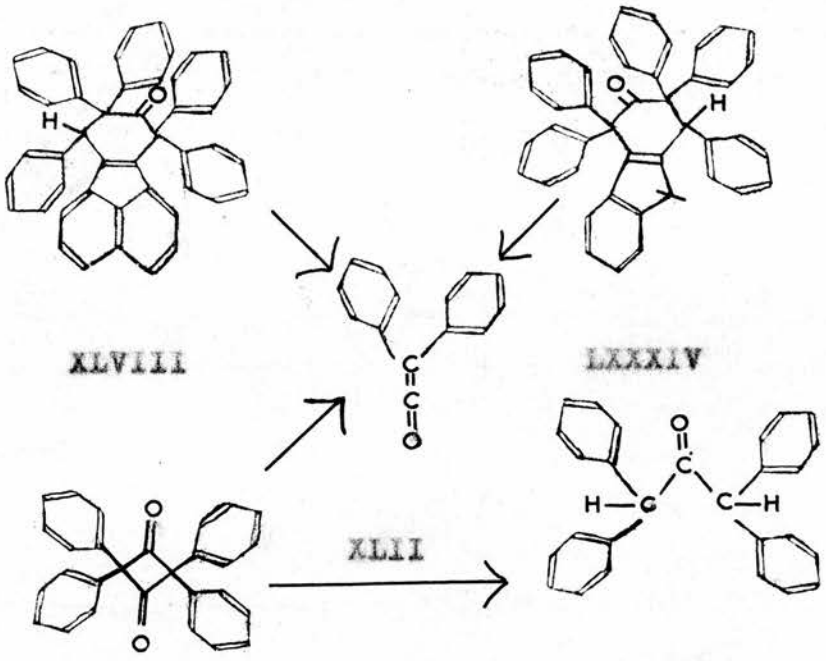
The dimer XLIX is formed by heating diphenylketene, which can be recovered again by heating the solid dimer.[260] It is of interest to note that an experiment to obtain diphenylketene from the then unrecognised compound of M.P. 245-6°C., by means of distillation in high vacuum at about 250 C. (see

Empirical Formula	Theoretical Analysis			Experimental Analysis			Possible Product	M.P. in °C.
	C%	H%	O%	C%	H%	O?%		
$C_{29}H_{22}$	94·0	6·0	0·0	93·2	5·8	1·0	LXXXIII	136·5
							LXXXVIII	-139
$C_{43}H_{32}O$	91·5	5·7	2·8	89·4	5·9	4·7	LXXXIV	228-9
							XCVI	
				(88·4	5·7	2·8)		230-
								231·5
$C_{28}H_{20}O_2$	86·6	5·2	8·2	86·4	5·3	8·3	XLIX	245-6
$C_{27}H_{22}O$	89·5	6·1	4·4	89·8	6·4	3·8	LXXVII	133·5
	(M.W.362·5)			(M.W.256)				-135
$C_{30}H_{22}O_2$	86·9	5·4	7·7				LXXXI	
$C_{32}H_{22}O$	91·0	5·3	3·8				Dimer	
$C_{29}H_{20}O$	94·5	5·5	0·0				XCI	

Table II

p. 196 for the method), led to the isolation of no diphenylketene (as the acetanilide)[127,157,143], but to the isolation of the unchanged starting material, suggesting that XLIX can be distilled in high vacuum (though not at atmospheric pressure)[260] without decomposition, and must therefore be more stable than compound XLVIII (p.180) and the compound believed to be LXXXIV (p.195), both of which decomposed to yield diphenylketene (XLII) under similar conditions of high vacuum distillation.

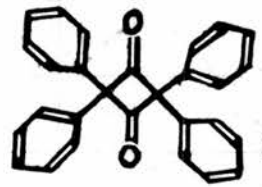
Confirmation of the identity of the compound



of M.P. 245-6°C. was ontained by its hydrolysis with a mixture of dil. NaOH, benzene and ethanol, which gave a good yield of fine colourless needles, M.P. 133·5-135°C., which corresponded in melting-point and analysis with sym-tetraphenylacetone (LXXVII, lit. M.P. 135°C.), described by Staudinger[260,282] as being the product of alkaline scission of XLIX. This was supported by the decolourisation of bromine in CCl_4 by the substance, though no 2:4-dinitrophenylhydrazone was obtained from it. The ultraviolet spectra of the compounds melting at 245-6°C. and 133·5-135°C. are shown on p. 85.

The third compound to be discussed, also from the interaction of 2-benzylidenehydrindene-3-one (LXXX) with excess diphenylketene (XLII), formed colourless crystals which melted at 228-9°C., with evolution of gas. The mode of formation of

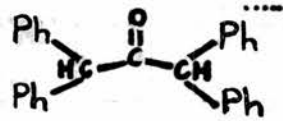
ULTRAVIOLET SPECTRA



2:2:4:4-TETRAPHENYLCYCLO-BUTANE-1:3-DIONE (XLIX),

1. QUALITATIVE IN CYCLOHEXANE (FROM CLEMMENSEN REDUCTION).

2. QUANTITATIVE IN ETHANOL (FROM REACTION OF 2-BENZYLIDENEHYDRO-INDENE-3-ONE & DIPHENYLKETENE).



SYM-TETRAPHENYLACETONE (LXXVII), IN CYCLOHEXANE.

$\text{Log}_{10}\,\epsilon$

5·4 5·2 5·0 4·8 4·6 4·4 4·2 4·0 3·8 3·6 3·4 3·2 3·0 2·8 2·6 2·4 2·2 2·0 1·8

200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430

λ m.μ.

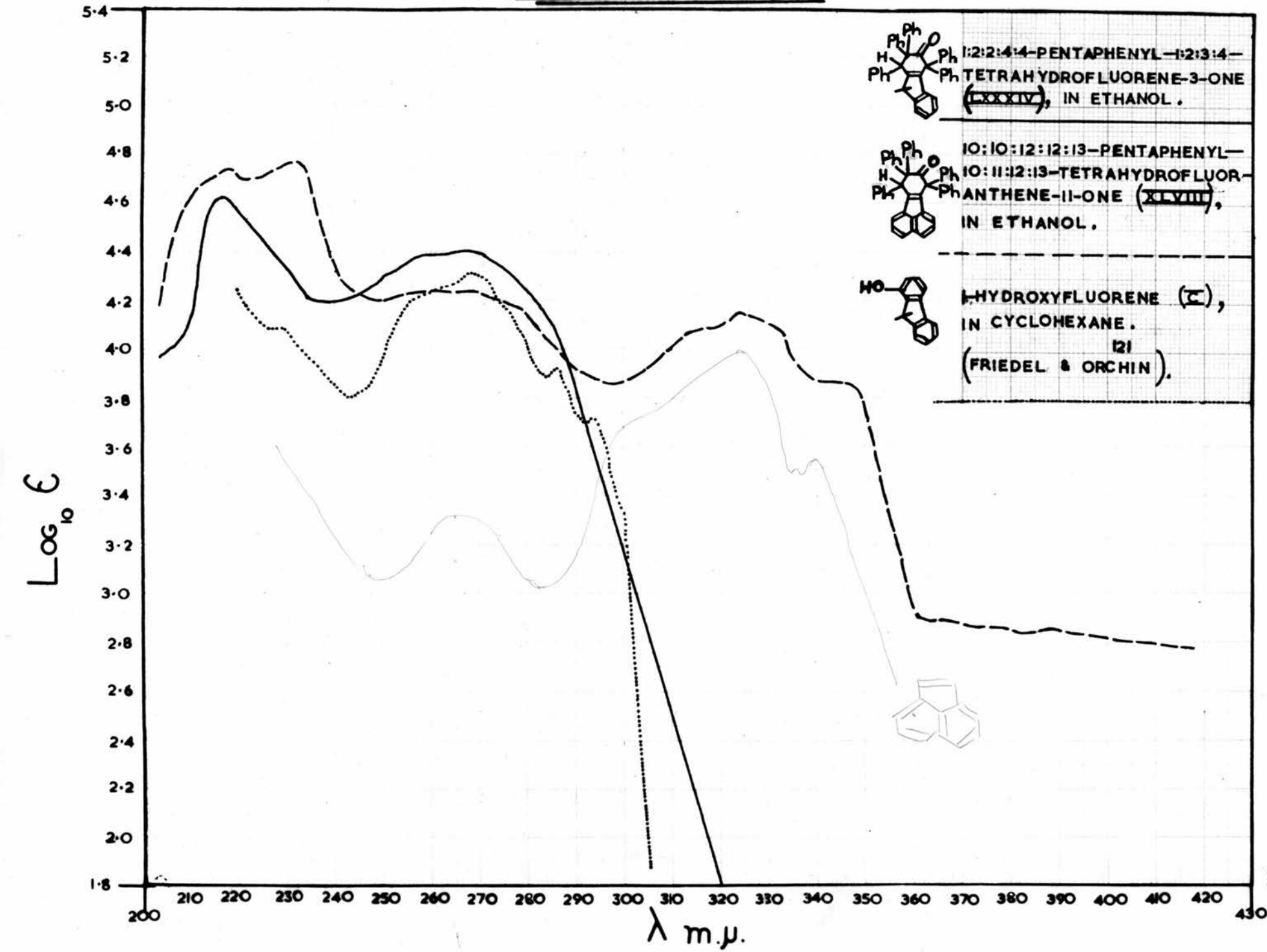
this compound resembled the synthesis of 10:10;12-12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII), which suggested that it might be the analogous compound 1;2:2:4:4-pentaphenyl-1:2:3:4-tetrahydrofluorene-3-one (LXXXIV), and analysis supported this. The compound (20mg.) was heated in high vacuum at about 250°C. (c.p. p. 50) and yielded diphenylketene (XLII), which was isolated, and identified by mixed melting-point, as diphenylacetanilide (5 mg.). The residue in the heating bulb yielded a few milligrammes of unchanged starting material, and a yellow uncrystalliseable oil.

127,157,143

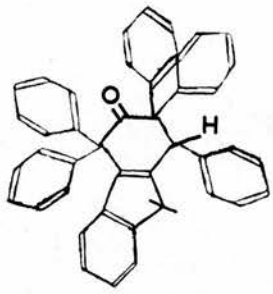
The product of M.P. 228-9°C. is, therefore, an adduct of diphenylketene and some other compound, and as no simple polymer of diphenylketene (XLII) has the composition required by analysis, formulae LXXXIV and XCVI represent the most likely structures for the compound, especially in view of the existence of the analogous fluoranthene derivative XLVIII. As in the case of the fluoranthene compound, steric considerations (p. 44) make it probable that the compound of M.P. 228-9°C. is 1:2:2:4:4-pentaphenyl-1:2:3:4-tetrahydrofluorene-3-one (LXXXIV). The spectrum of this compound is shown on p. 87 along with that of 10;10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII), with which it has some points of similarity, and that of 1-hydroxyfluorene (C), which it strongly resembles, and which confirms that it is a

121

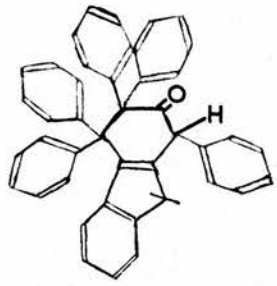
ULTRAVIOLET SPECTRA



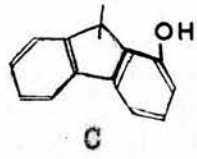
fluorene derivative.



LXXXIV



XCVI

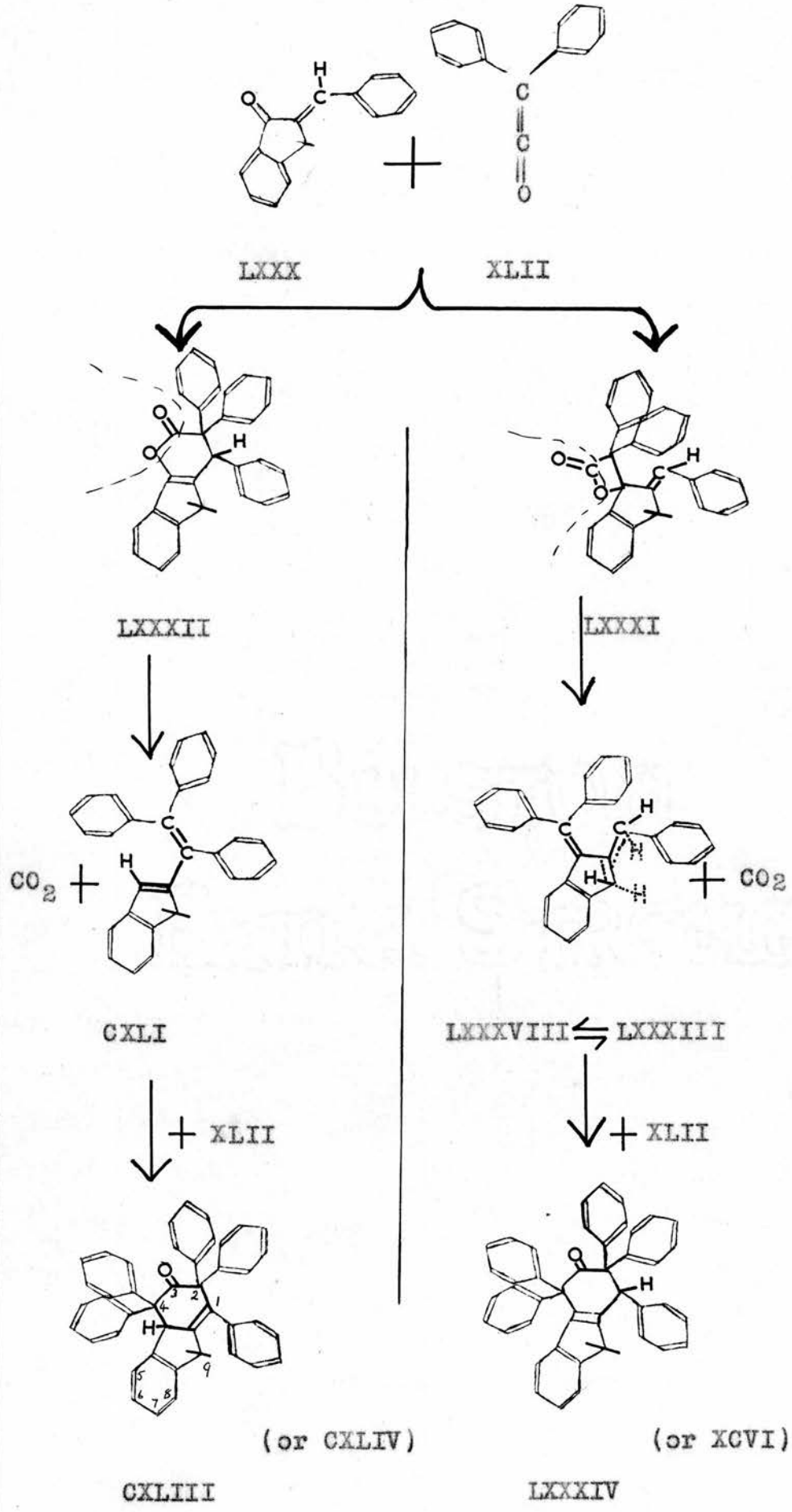


C

No compound corresponding in analysis to 1:4-diphenyl-2:3-benzfluorene (XCI, p. 76) was found.

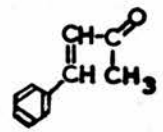
Here, as in the reaction between 7-benzylideneacenaphthene-8-one (IV) and diphenylketene (XLII), the possibility of the initial formation of a δ-lactone LXXXII must be considered. The series of products to which a δ-lactone would be expected to give rise is shown in Scheme O alongside the formulae of the corresponding isomeric β-lactone derivatives.

In this case, as none of the products are available from other sources and no ring-closure occurred to form XCI (p. 76), no direct proof of structure can be given. The facts that the compound 2-indenyltriphenylethylene (CXLI) cannot tautomerise, and as it is not a fulvene derivative,

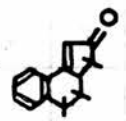

LXXX
XLII
LXXXII
LXXXI
CXLI
LXXXVIII ⇋ LXXXIII
+ XLII
+ XLII
(or CXLIV)
(or XCVI)
CXLIII
LXXXIV

Scheme O

ULTRA-VIOLET SPECTRA



BENZYLIDENEACETONE (CXLVIII),
IN ETHANOL.
(WILDS *et alia*.[148])



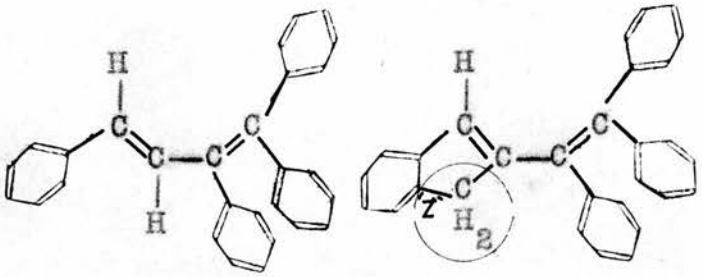
$\Delta^{1:1'}$-2'-KETO-3:4-DIHYDRO-1:2-CYCLOPENTENONAPHTHALENE (CXLIX),
IN ETHANOL.
(WILDS *et alia*.[148])

$\log_{10} \varepsilon$

5·4 5·2 5·0 4·8 4·6 4·4 4·2 4·0 3·8 3·6 3·4 3·2 3·0 2·8 2·6 2·4 2·2 2·0 1·8

200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430

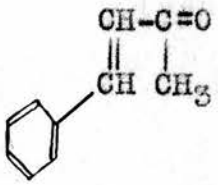
λ m.μ.



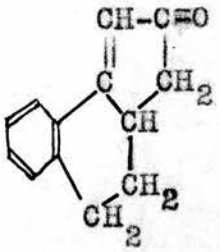
XLIII CXLI

is unlikely to be yellow, suggest, however, that the formula CXLI does not account for the formation of a yellow solution and melt from the colourless crystals of the compound of M.P. 136·5-139°C. Furthermore, it should be noted that methylene groups forming rings such as the group 'z' in CXLI, which distinguishes CXLI from 1:3:4:4-tetraphenylbutadiene (XLIII), would be expected to make very little difference to the spectrum of the compound, and the spectrum of CXLI would therefore be expected to very closely resemble that of XLIII. Though there are resemblances between the spectra of the compound of M.P. 136·5-139°C. and that of XLIII (p. 57), the similarity is not nearly as strong as would be expected from the similarity of, for example, the spectra of benzylideneacetone (CXLVIII) and $\Delta^{1:1'}$-2'-keto-3:4-dihydro-1:2-cyclopentenonaphthalene, CXLIX, (p. 90[148]).

Thus it is probable that the initial adduct is again the β-lactone, and that the compound of M.P. 136·5-139°C. is 3-diphenylmethylene-2-benzylidenehydrindene (LXXXIII) or its tautomer LXXXVIII. As the compound of M.P. 228-9°C. is



CXLVIII



CXLIX

assumed to be formed from LXXXIII, it follows that this is 1:2:2:4:4-pentaphenyl-1:2:3:4-tetrahydrofluorene-3-one (LXXXIV), and not 1:2:2:4:4-pentaphenyl-2:3:4:5-tetrahydrofluorene-3-one (CXLIII) (or 1:2:2:3:3-pentaphenyl-2:3:4:5-tetrahydrofluorene-4-one, CXLIV).

Summary of the Action of Diphenylketene on α:β-Unsaturated Aromatic Ketones

The effects of treating 7-benzylideneacenaphthene-8-one (IV) and 2-benzylidenehydrindene-3-one (LXXX) with diphenylketene (XLII) under various conditions have been discussed, and the reactions believed to occur are shown in black in Schemes M and N (p. 76-7), and before continuing with the two exploratory sections of Part I of this Thesis, the results of this first section will be summarised.

In both reactions, a diphenylmethylene derivative is believed to be formed, as might be expected from Staudinger's work with aromatic ketones[179,180], and as these intermediates are substituted butadienes, each appears to be able to react with excess diphenylketene to produce a highly phenylated cyclic adduct (XLVIII and LXXXIV), which can be relatively readily decomposed into the starting materials on heating, being comparable in this respect with the dimer of diphenylketene, XLIX.

There is, however, one striking difference between the behaviour of these aromatic α:β-unsaturated ketones and Staudinger's chalkones[123,126]. Though in none of the experiments carried out for this section could a β- or δ-lactone derivative be isolated, the course of the reactions showed that a β-lactone either had been formed (XLIV), or was very likely to have been formed (LXXXI). It

therefore appears as if the aromatic α:β-unsaturated ketones IV and LXXX behave like simple ketones, such as fluorenone, rather than like the α:β-unsaturated ketones studied by Staudinger. Further attempts to prepare fluoranthenes containing a lactone oxygen atom are described in Part II, Section 6 of this Thesis, and the reasons for their failure are discussed on p. 153.

Lastly, the striking difference between the series of reactions undergone by 7-benzylideneacenaphthene-8-one (IV) and 2-benzylidenehydrindene-3-one (LXXX) is the failure of the latter to produce an aromatic hydrocarbon XCI, (p. 76) equivalent to 10:13-diphenyl-11:12-benzfluoranthene (LXIV). Two possible reasons suggest themselves for this. Firstly, the rigid planar configuration of the 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) molecule and the overcrowding of its substituents force the ortho hydrogens of one of the diphenylmethylene phenyl groups into very close proximity to the active hydrogen of the benzylidene group, probably closer than in the case of the less predominantly aromatic derivative LXXXIII. Secondly, in the case of the acenaphthene derivative the active hydrogen is relatively rigidly fixed to the benzylidene carbon, while in 3-diphenylmethylene-2-benzylidenehydrindene (LXXXIII) the possibility of isomerisation to form a benzyl derivative introduces free rotation about the bond attaching the benzyl group to the indene ring, and this will reduce the tendency to lose

hydrogen, just as it would have prevented its loss from the hypothetical CXLI.

Section II

The Use of Ketene and Phenylketene

In view of the fruitful outcome of the investigations with diphenylketene, it was decided to carry out exploratory experiments with other ketenes (see Scheme P, p.100, and compare with Schemes M, N and J, ps. 76, 77 and 62).

The ketenes used were ketene itself (CIX), which is relatively readily handled and the preparation of which is described on p.202, and the extremely unstable phenylketene (CX), the preparation of which is described on p.198.

The first experiments were carried out by heating phenylketene (CX) solution with chalkone (XVI) or 7-benzylideneacenaphthene-8-one (IV) at 120-140°C., and in both cases a red - black coloured tar was formed. Attempts to crystallise the tars were unsuccessful, though in both cases an intensely coloured solution was produced.

In the reaction between phenylketene (CX) and 7-benzylideneacenaphthene-8-one (IV), no pure compound was isolated, but chromatography of the red tar provided some information which may be of use to later investigators, and is detailed on p. 199. The most interesting fractions of the eluate were:

1. A brown solution, eluted with petrol (B.P. 80-100° C.), with a striking blue fluorescence

in ultra-violet light, which suggested that this might contain 7:8-dibenzylideneacenaphthene (LVIII).

2. A clearly defined black band which was left on the column after elution with benzene, and was extracted with ether in a Soxhlet extractor. This afforded an intensely coloured solution which was deep red when acid, but in alcohol, or toluene that had been standing over sodium, became a dark blue-green colour verging on black, which was changed to yellow by NaOH solution. Attempts to obtain crystals from this solution with acetone were unsuccessful, and rechromatographing in dioxan was also unproductive. The rechromatographed residues were dissolved in phosphoric acid and petrol, and gave a cherry red colour in the acid layer which on dilution became blue and gave a slight precipitate, but no crystalline product was isolated.

In the reaction between chalkone and phenylketene, a crystalline product was obtained. The red tar initially produced would not crystallise and the benzene soluble part of the tar was chromatographed on alumina. Development of the chromatogram with 50% petrol in benzene and elution with benzene yielded oils from which no crystals were obtained. Elution with ether, however, removed a maroon band from the column, which on crystallisation from acetone gave deep red, almost black needles with a golden lustre, which had a

melting-point of 236-8°C. No other crystalline product was obtained, though there were several unresolved fractions.

The colour of this red compound was also dependent on the acidity of the solution and on the solvent. In chloroform it was red-violet (violet in aqueous-acetone), which on addition of a drop of acid became red (yellowish in aqueous-acetone), this change being reversed by the addition of ammonia.

Analysis of the compound corresponded more closely with the composition of an adduct of one mol. of phenylketene (CX) and one mol. of chalkone (XVI) than with that of a polymer of phenylketene (Table IV). The dark colour of the solution unfortunately prevented the determination of the molecular weight.

Possible Products	Theoretical Analysis			Experimental Analysis		
	C%	H%	O%	C%	H%	O(?)%
1mol. Chalkone plus 1mol. CX	84·6	5·6	9·8	87·0	4·7	8·3
Dimer of CX	81·3	5·1	13·5			

Table IV

In view of the small yields of pure product, and the apparent complexity of these reactions with phenylketene (CX), the reactions of the more

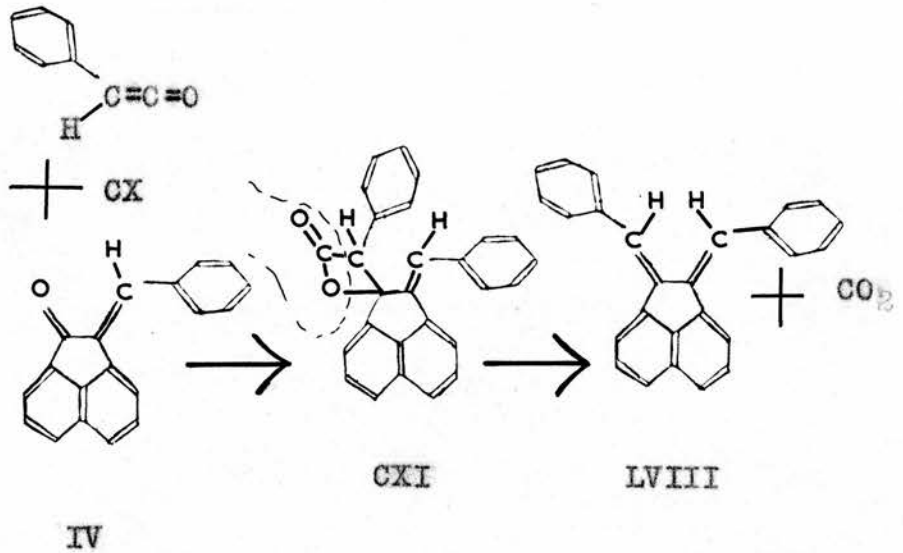
easily handled ketene (CIX) were investigated, but these proved much less productive than those with phenylketene.

Several attempts were made to cause a reaction by passing ketene (CIX) through chalkone (XVI) in acetone solution using temperatures varying up to over 200°C. In no case could any product other than unchanged chalkone be obtained, and even in a reaction carried out at 200°C., apart from a small residue with a blue ultra-violet fluorescence, the starting material appeared unchanged.

It was thought that the zinc chloride, which was likely to be present in the phenylketene (CX) solution as an impurity, might be partaking in forming the red compounds, and reactions were therefore tried in the presence of zinc chloride with ketene (CIX) and chalkone (XVI), and with diphenylketene (XLII) and 7-benzylideneacenaphthene-8-one (IV), but no red coloured compounds appeared.

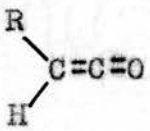
Several other reactions using ketene (CIX) and diphenylketene (XLII) in the presence of catalysts were tried, but as they were aimed at producing oxofluoranthene derivatives (p.150), they are included in Part II of this Thesis. One of these reactions, however, should be mentioned here. It was found that when chalkone (XVI) was treated with ketene (CIX) in the presence of boron trifluoride catalyst, a bright red colour was produced, and though no pure product was isolated, the red substance resembled the red compounds produced with phenylketene (CX) in so far as it was soluble in

acetone, dioxan, and phosphoric acid, and gave intensely red solutions.

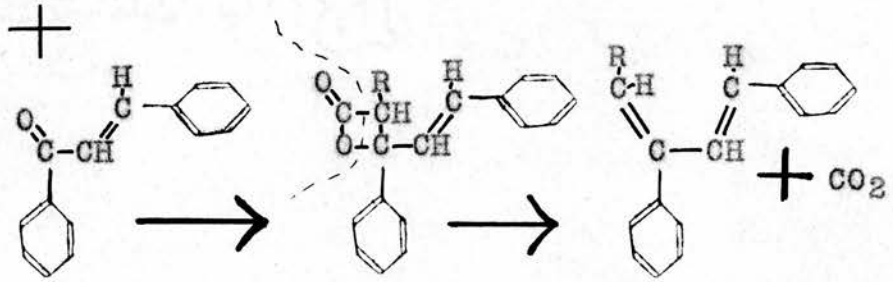


IV CXI LVIII

('R' can be phenyl or hydrogen)



CX or CIX



XVI CXII CXIII

Scheme P

The aim of these exploratory experiments was to produce derivatives of 7:8-dibenzylideneacenaphthene (LVIII), but, except for the solution with a blue fluorescence mentioned on p. 96 para. 1, which probably contained a small quantity of LVIII, or a derivative of LVIII, there was no evidence that the

reaction was likely to provide a useful synthesis of LVIII.

The red coloured products were more interesting, and the fact that they were produced with:

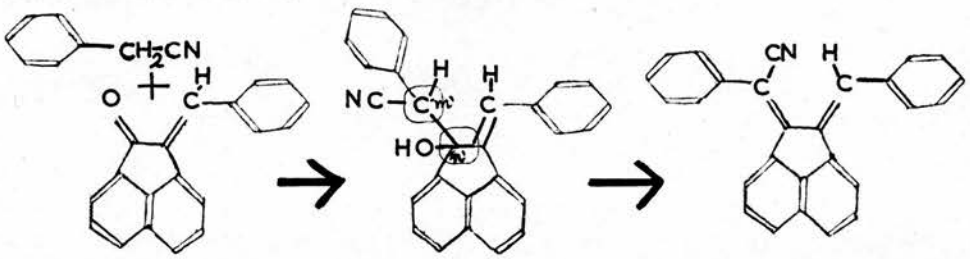
1. Phenylketene and chalkone,
2. Ketene and chalkone (in the presence of BF_3),
3. Phenylketene and 7-benzylideneacenaphthene-8-one,

suggests that a whole series of coloured compounds might be produced by the interaction of ketenes with α:β-unsaturated ketones. Ketenes are known to form strongly coloured dimeric derivatives[125,146,167], but the analysis of the product of the reaction between chalkone and phenylketene, and the fact that the derivative of phenylketene with IV was somewhat bluer in colour than that with chalkone, while that produced with ketene was somewhat redder than the others, would suggest that these compounds were not dimers of the ketene or of the ketone. Possible structures for these compounds are put forward on p. 155. Other coloured ketene derivatives are known[163], e.g. with acetophenone and benzilic acid, and some of their structures and the structures of the ketene dimers appear from the literature to be uncertain[125,146,163-8,172,173,274], therefore these reactions were not pursued further, as they might in themselves provide the subject matter for a whole thesis.

Section 3

Condensation with Benzyl Cyanide

In an attempt to prepare congeners of 7:8-dibenzylideneacenaphthene, the condensation of benzyl cyanide (CXLV) with 7-benzylideneacenaphthene-8-one (IV) was studied.[186,192,255]



CXLV & IV CXLVI CXLVII

It was found that by condensing the ketone (IV) with benzyl cyanide (CXLV) in the presence of potassium ethoxide, up to 59% yields of a colourless crystalline product of M.P. 190-215°C. could be obtained. This product was not a pure single compound, and was composed of a mixture of a compound forming prismatic crystals and one forming needles. These were separated by hand, with difficulty by crystallisation, and by carefully heating the mixed crystals on a piece of filter-paper on the hot stage of a Kofler microscope until the lower melting fraction melted and was absorbed by the filter paper. By each of these methods, small and rather impure specimens of the products were obtained. The prismatic form melted at 204-8°C. and the needle shaped form at 218-221°C.

while a mixed melting-point between the two forms started to melt at 195°C., showing that they were in fact different compounds.

Analysis of specimens of both forms corresponded with the theoretical analysis of 7-benzylidene-8-(w-cyanobenzyl)-acenaphthene-8-ol (CXLVI), suggesting that they were isomers. This is not surprising as this molecule contains two asymmetric carbon atoms "m" and "n", and can exist in optically active or racemic forms.

It was hoped that by dehydration of the mixed condensation products, w-cyano-7:8-dibenzylideneacenaphthene (CXLVII) might be produced, and that even though this compound can form geometric isomers, one at least of these would be easily isolable as a pure compound. Attempts to obtain these by dehydration with formic acid, dry HCl, $KHSO_4$, and P_2O_5 were unsuccessful, as analysis of the final products suggested that these still contained oxygen, and the principal reaction product formed a 2:4-dinitrophenylhydrazone.

The reaction conditions used were rather vigorous, and a number of other reactions are conceivable under them, these include; the possibility of a transformation similar to that noted by Beschke[265] with acenaphthene glycols (p. 46), the possibility of hydration of the nitrile (with the water generated by the dehydration) to form an amide as nit-

riles are hydrated in this manner with 96% H_2SO_4,[275] and the possibility of a polymerisation or an internal ring-closure involving the nitrile group.[187,188,189,190] In one experiment, a product was isolated the composition of which suggested it might be a nitrilium halide.[191]

Analyses of the principal product of the dehydrations showed this to have a composition similar to but distinct from that of CXLVI, and as it yielded a 2:4-dinitrophenylhydrazone, it could not be CXLVI, and must be some unidentified derivative of this compound. In view of failure to prepare CXLVII and the difficulty of isolating pure compounds, this work was discontinued.

DISCUSSION

PART II

THE REACTIONS OF

7-BENZYLIDENEACENAPHTHENE-8-ONE

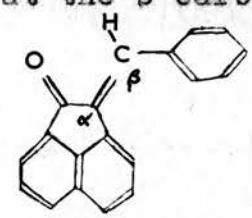
AND THE PREPARATION OF 10-PHENYL-

FLUORANTHENE DERIVATIVES

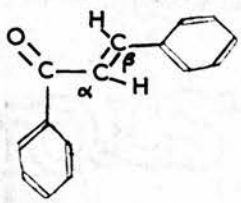
Section IV

Condensation Reactions

α:β-Unsaturated carbonyl compounds, of which α:β-unsaturated ketones such as chalkone (XVI) and 7-benzylideneacenaphthene-8-one (IV) are only one example, are notable for their reactivity, and especially for the ease with which condensation reactions occur at the β carbon atom. Additions can



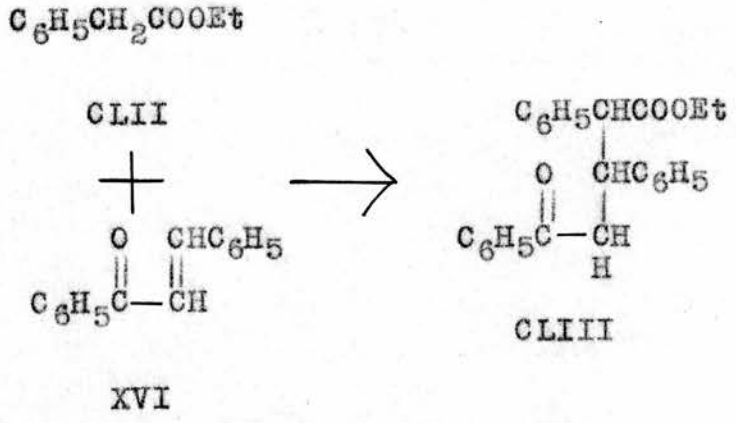
IV



XVI

occur to the chalkone system with various types of compound, some of which are listed on p. 163. One of the most important of these reactions is the condensation of chalkones with acetoacetic ester (CLI) and similar compounds, and exploratory experiments had been carried out[57] with 7-benzylideneacenaphthene-8-one (IV) and this reagent, but had not been studied systematically. These interactions are base catalysed Michael condensations[215,224] and occur between α:β-unsaturated ketones and compounds, such as acetoacetic ester (CLI), containing a hydrogen atom activated by a ketonic, ester, nitrile or nitro grouping, and thus behaving as a proton donor. The proton donor adds on to the β position of the

unsaturated carbonyl compound and the active hydrogen moves to the α-position, as, for example, in the reaction between chalkone (XVI) and phenylacetic ester (CLII) to form α:β-diphenyl-γ-benzoylbutyric ester (CLIII).[216] A detailed discussion of the mechanism of the Michael reaction is to be found in the standard textbooks.[217]



Michael's original experiments used molar quantities of reactants and of sodium ethoxide,[215] however, variations of these have been developed by Knoevenagel,[208,218,224] in which a secondary amine such as diethylamine or piperidine is used as catalyst, and by Kohler[209] whose method uses only catalytic quantities of sodium ethoxide. Acid catalysed reactions based on the Michael reaction, which involve the addition of water or alcohols to an α-β double bond conjugated to a carbonyl or carboxylic grouping, are also known,[217,219,277] and in many cases are reversible.

The following pages contain descriptions of

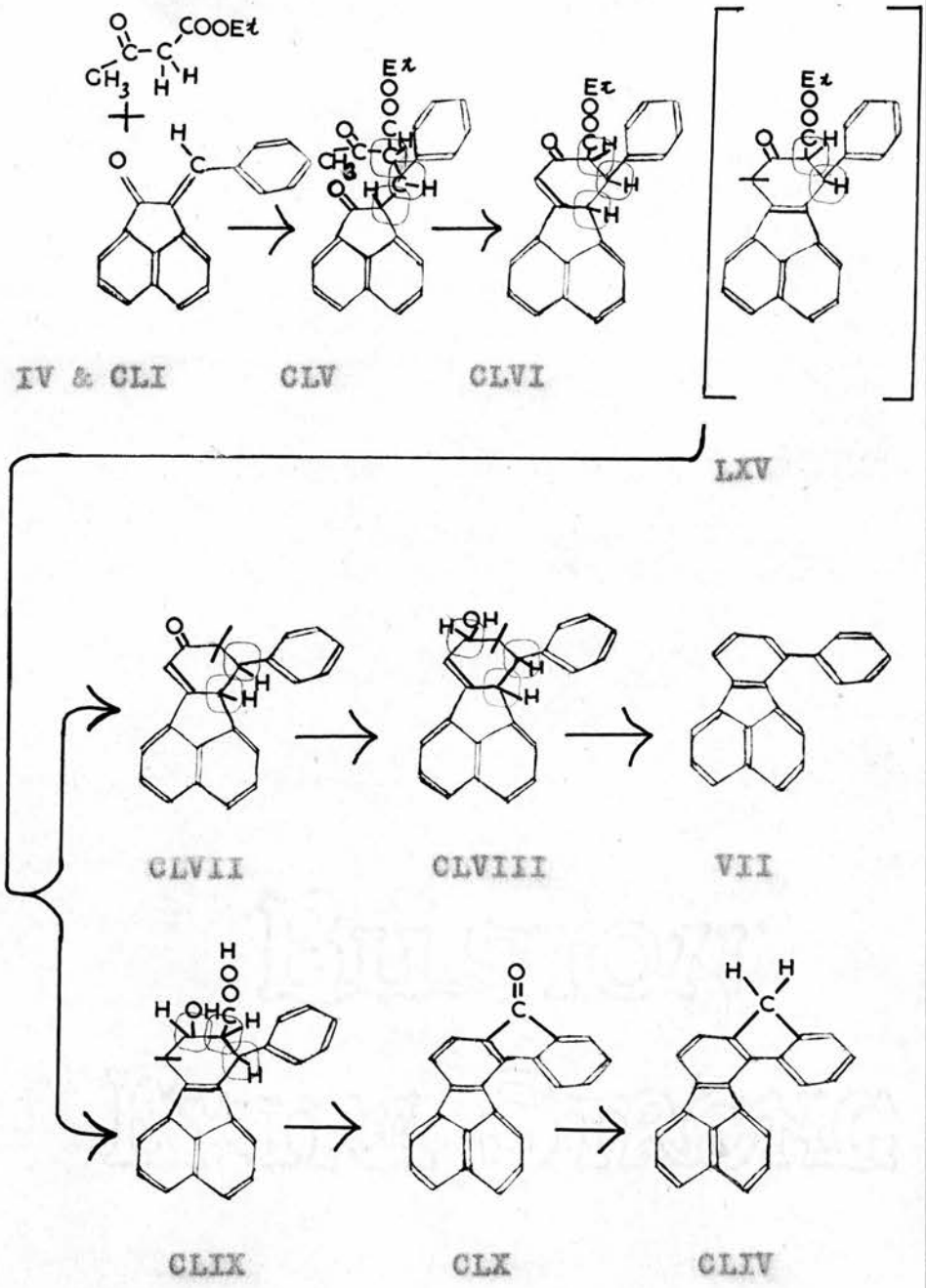
the condensation of 7-benzylideneacenaphthene-8-one (IV) with acetoacetic ester (CLI), α:γ-diphenylacetoacetic ester (CLXII), and sym-tetraphenylacetone (LXXVII), and of the products obtained from these condensations.

CH_3COCH_2COOEt	$PhCH_2COCHCOOEt$ (Ph on CH)	$Ph_2CHCOCHPh_2$
CLI	CLXII	LXXVII

Condensation of 7-Benzylideneacenaphthene-8-one with Acetoacetic Ester

This Michael reaction was used with the intention of carrying out the series of reactions shown in Scheme S and thus preparing 10-phenylfluoranthene (VII) and, as a secondary aim, indeno-(3':2'-10:11)-fluoranthene (CLIV). Neither of these hydrocarbons was in fact isolated though a compound believed to be 10-phenylfluoranthene-12-borate (CLXIII) was obtained, and, although the initial condensation went smoothly and gave fair yields, the later stages gave poor yields, and when the carbonyl group had been reduced to a hydroxyl group, oils were obtained which were difficult to crystallise. It will be noticed from Scheme S that many of the compounds involved contain asymmetric carbon atoms, shown emboxed in the Scheme, and the creation of a new asymmetric centre by the reduction of the carbonyl group to form CLVIII and CLIX thus increased the number of isomers present, and was probably responsible for preventing crystallisation and hence the effective purification of the products.

The Michael condensation with 7-benzylideneacenaphthene-8-one (IV) and acetoacetic ester (CLI) was carried out by the method used by W.H. Stafford[57] in his exploratory work, with sodium in ethanol as catalyst. The principal product of this reaction formed canary yellow granular crystals of M.P.



Scheme S

180-181·5°C., and on careful examination of the mother liquors, pale yellow needles of a second compound, M.P. 160-2°C., were obtained in small yield. Analyses of these compounds (Table VII) suggested that both were probably isomeric with CLVI, and that the primary product of the condensation (CLV) had ring-closed spontaneously under

the reaction conditions. Various catalysts and variations in the experimental conditions were tried and are summarised in Table VIII p.114, and yields of up to 64% of the compound of M.P. 180-181·5°C. were obtained. Only small quantities of the compound of M.P. 160-2°C., which was insoluble in sodium carbonate solution and therefore not likely to be an acid derivative of LXV or CLVI, were isolated, and attempts to confirm the structures of these compounds were therefore largely limited to the high melting-point product. As

Empirical Formula	Theoretical Analysis			Experimental Analysis			Possible Product	M.P. °C.
	C%	H%	O%	C%	H%	(O%)		
$C_{25}H_{20}O_3$	81·5	5·5	13·0	81·0	5·7	13·3	LXV	180-181·5
				79·4	5·1	15·5	CLVI	160-162
$C_{25}H_{22}O_4$	77·7	5·7	16·6				CLV	
$C_{23}H_{16}O_3$	81·2	4·7	14·1				CLXI	

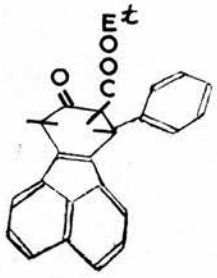
Table VII

the synthesis of these products was unambiguous, the general outline of their structures seems clear despite the poor analysis of the compound of M.P. 160-2°C., but this is discussed in more detail on p.123 et seq.

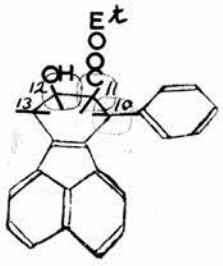
Attempts were next made to reduce the carbonyl group of the high M.P. compound by the Clemmensen 158-160

and the Wolff-Kishner techniques and by the use of potassium borohydride, but these reactions proved difficult and did not yield the expected products (see p. 217).

No crystalline product was obtained from the reduction with potassium borohydride, presumably because of the generation by the reduction of a new asymmetric centre in the 12 position of CLXV, but



LXV

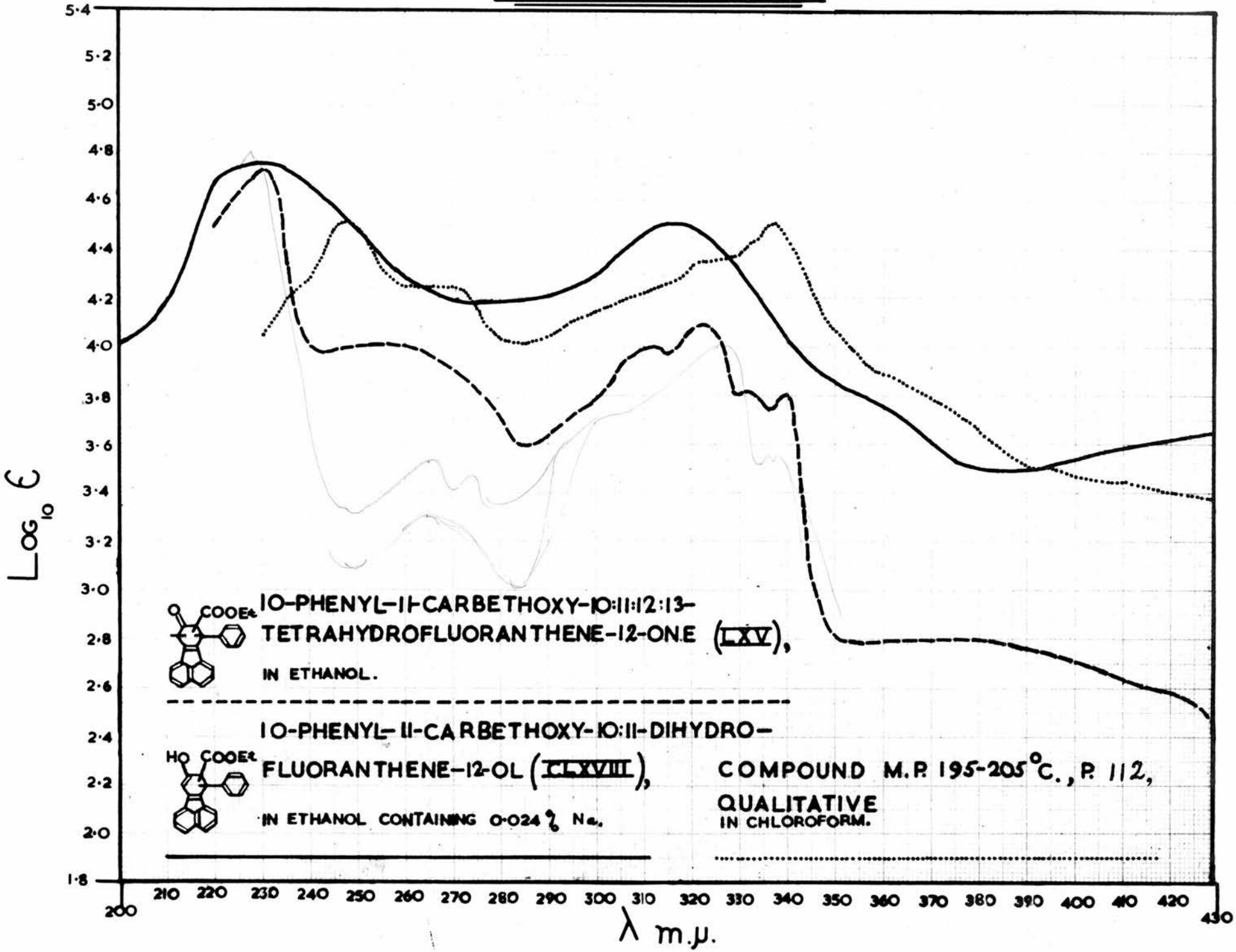


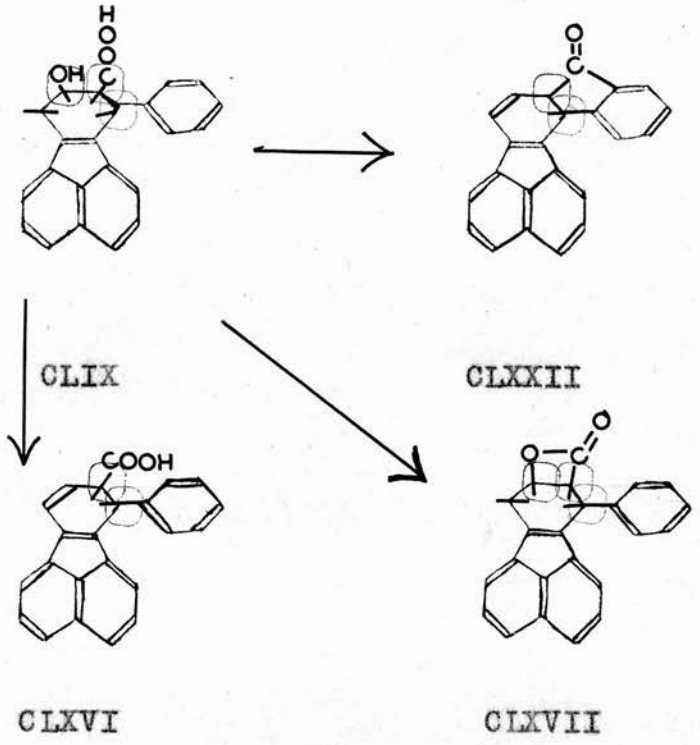
CLXV

part of the oil from the reduction proved to be acidic and was assumed to contain 10-phenyl-11-carboxy-10:11:12:13-tetrahydrofluoranthene-12-ol (CLIX, see p. 220), and exploratory attempts were made to dehydrate this with phosphorus pentoxide in the hope of producing 1'-oxo-indeno-(3':2'-10:11)-10:11-dihydrofluoranthene (CLXXII, Scheme T).

Only very small quantities of a crude product of M.P. 195-205°C. were isolated from these reactions, and analysis suggested that this was either the acid CLXVI or the δ-lactone CLXVII, or a mixture of these, all of which could be formed in theory by the reaction (see Scheme T and Table VIII). The qualitative ultra-violet spectrum of the crude compound of M.P. 195-205°C. is shown on p. 113, and resembles more closely that of

ULTRAVIOLET SPECTRA





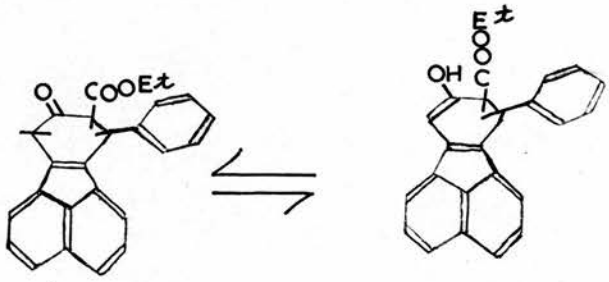
Scheme T

Compound	Theoretical Analysis			Experimental Analysis		
	C%	H%	O%	C%	H%	(O%)
CLXII $C_{23}H_{14}O$	90·2	4·6	5·2			
CLXVI $C_{23}H_{16}O_2$	85·2	5·0	9·9	86·6	4·3	9·1
CLXVII $C_{23}H_{16}O_2$	85·2	5·0	9·9			

Table VIII

10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one (LXV, see p. 113) observed in ethanol containing 0·024% of sodium, when the solution would be expected to contain a proportion of

10-phenyl-11-carbethoxy-10:11-dihydrofluoranthene-12-ol (CLXVIII, see p.128), than it resembles the spectrum of LXV in pure solvent. The spectrum of LXV in the presence of alkali is likely to be similar to those of CLXXII and CLXVI.



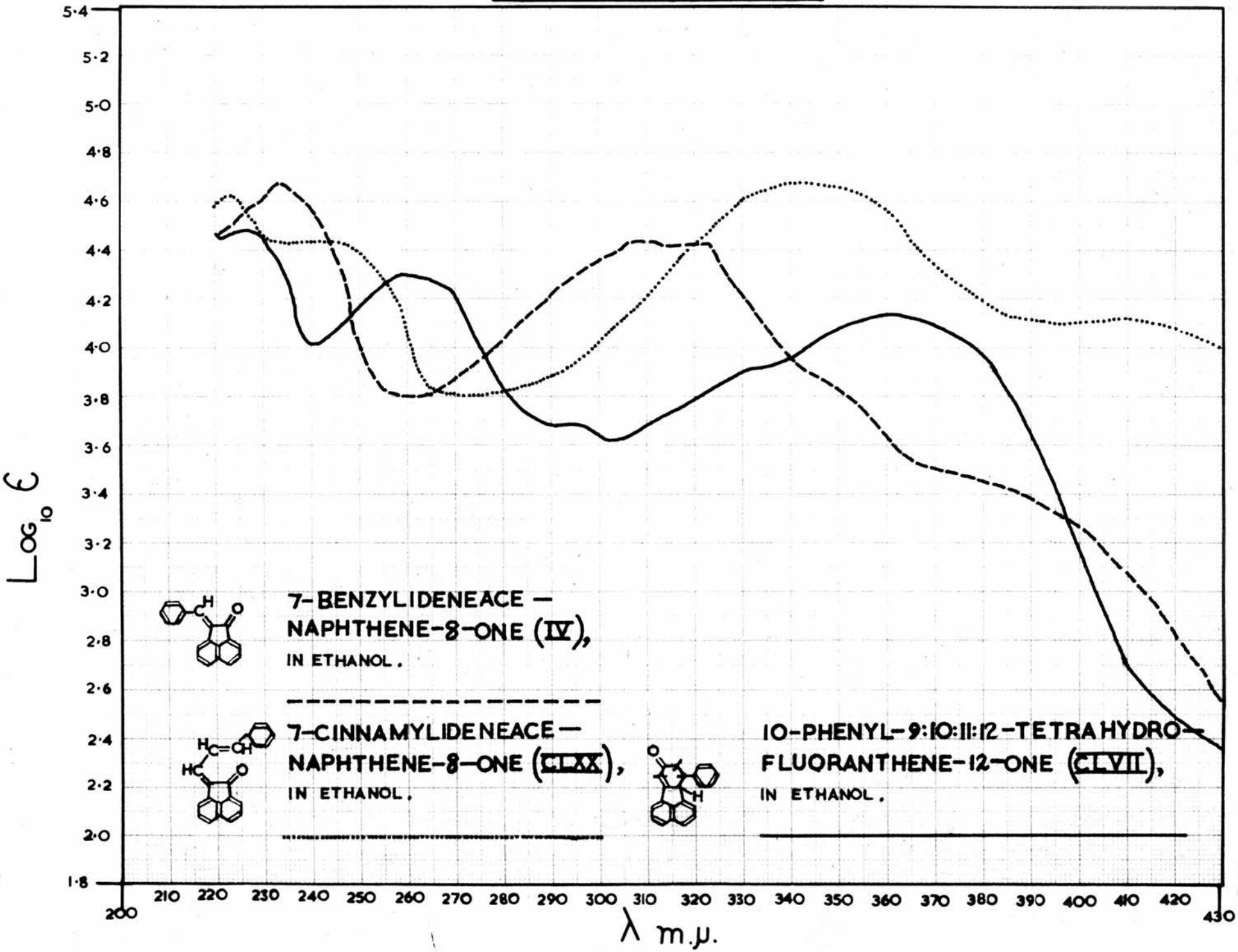
LXV CLXVIII

Since attempts to remove the ketonic substituent from LXV had been unsatisfactory, the compound was boiled under reflux with glacial acetic acid, water and sulphuric acid with the intention of removing the carbethoxy group by combined hydrolysis and decarboxylation. In two experiments, 50% and 39% yields of a compound, which on recrystallisation from benzene-petrol mixture melted at 187-9°C., and which formed a 2:4-dinitrophenylhydrazone, were obtained. Analysis of this compound confirmed that it was the expected 10-phenyl-9:10:11:12-tetrahydrofluoranthene-12-one (CLVII), or its acenaphthylene isomer (CXCV).

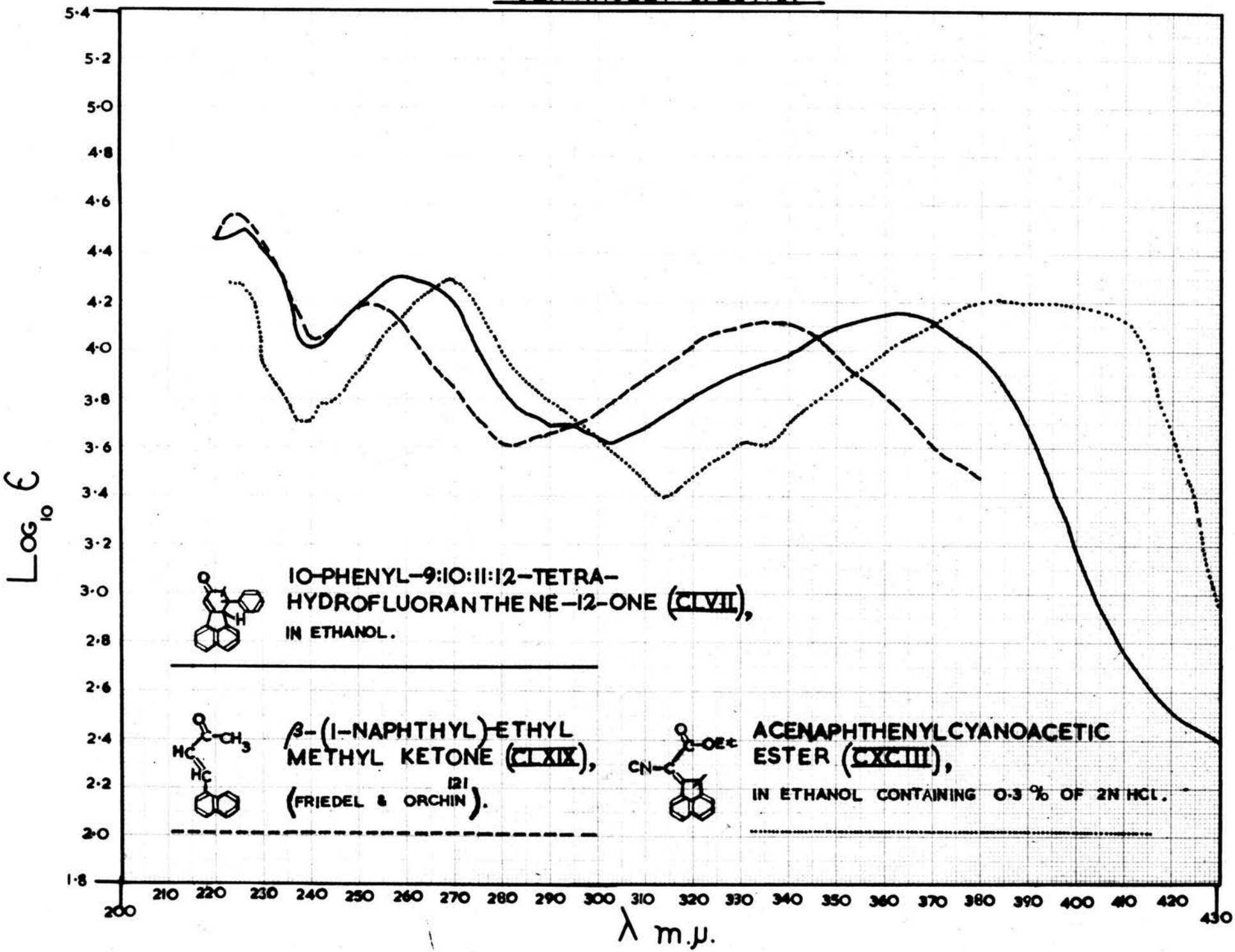
p. 224, two analyses figures

The ultra-violet spectrum of this compound is shown on p.117 along with those of β-(1-naphthyl)-ethyl methyl ketone (CLXIX) and acenaphthenylcyanoacetic ester (CXCIII), which it resembles, and on p.116 it is shown with the spectra of 7-cinnamylideneacenaphthene-8-one (CLXX) and 7-benzylideneace-

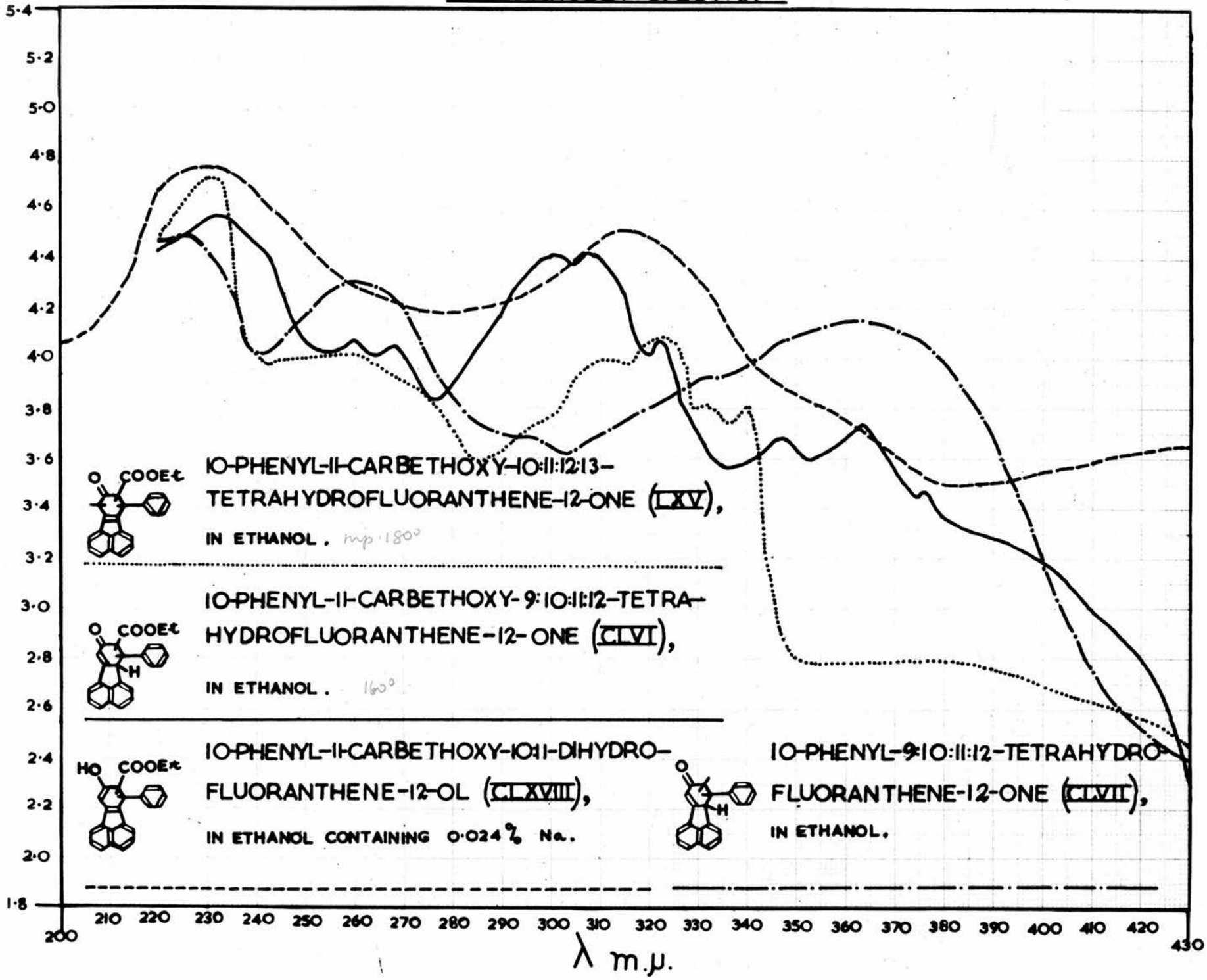
ULTRAVIOLET SPECTRA



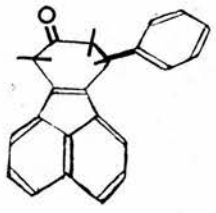
ULTRAVIOLET SPECTRA



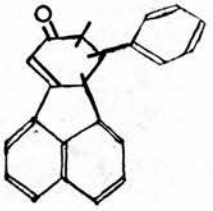
ULTRAVIOLET SPECTRA



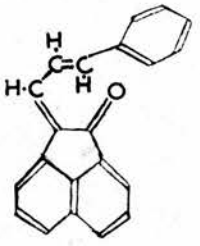
naphthene-8-one (IV), which it resembles in its lack of fine structure. On p.118 the spectrum of CLVII is shown along with those of LXV and CLVI, and the lack of the characteristic shape of the spectrum of the acenaphthylenic compound LXV is evident. Together, this information suggests that the compound melting at 187-9°C. exists in the acenaphthenyl form (CLVII), rather than the acenaphthylenic form (CXCV) which would be expected since it is formed from LXV (p.123).



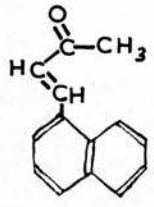
CXCV



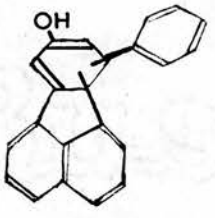
CLVII



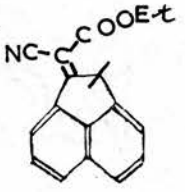
CLXX



CLXIX



CLXXI



CXCIII

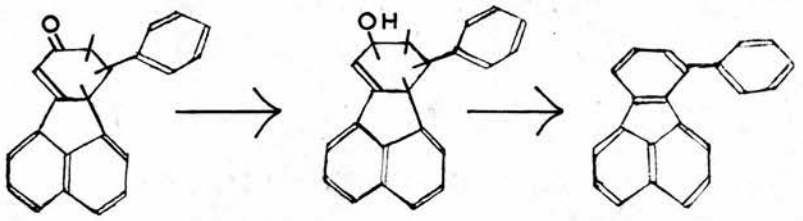
In general appearance, the spectrum of CLVII is more like the spectra of LXV and CLVI in ethanol containing sodium ethoxide than their spectra in the pure solvent (p.118), and suggests that some enolisation to form CLXXI might be occurring.

Reduction of the carbonyl group in CLVII with potassium borohydride yielded an oil with a green

220,226

P.224

fluorescence in ultra-violet light. Attempts to crystallise this failed, and the oily residues were therefore heated with a palladium on charcoal catalyst in the hope that, although the intermediate CLXXIII would not crystallise, probably because it was composed of a mixture of stereoisomers, the more symmetrical 10-phenylfluoranthene (VII), which can exist in only one form, might be obtained.



CLVII CLXXIII VII

Extraction of the residual solid with benzene, after heating the oil for half-an-hour up to 280°C. with palladium on charcoal, gave a dark green fluorescent solution suggesting the presence of a fully aromatic compound. After purification by chromatography, this gave a yellow solution with a bright green fluorescence which on crystallisation from benzene deposited bundles of very fine yellow needles of M.P. 199-202°C. The melting of this compound was rather peculiar because the viscous melt solidified on increasing the temperature and remelted at 321-3°C., and the high melting-point product, which was present in the crude substance, was extremely difficult to separate completely from the compound melting at 199-202°C. The two compounds were isolated, and a mixed melting-point

observed, but this showed no depression. The ultra-violet spectra of the two compounds were observed, and are practically identical and show them to be closely similar in structure, and the shape of these spectra suggests that the compounds were substituted fluoranthenes (cp. the spectrum of 10:11-benzfluoranthene, CIV, p. 125).

Analysis of the compound of M.P. 321-3°C. showed this to contain a large residue, precluding the possibility of its being 10-phenylfluoranthene (VII), and comparison of the analysis with those of other likely reaction products suggested that the compound contained a borate residue from the potassium borohydride reduction (Table IX).

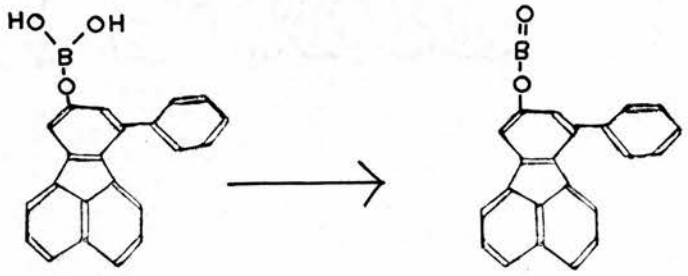
Compound	Theory. Analysis			Expt. Analysis		
	C%	H%	O+B%	C%	H%	O+B%
VII ($C_{22}H_{14}$)	94·9	5·1	0·0			
CLXXIII ($C_{22}H_{18}O$)	88·6	6·1	5·4			
CLXIII ($C_{22}H_{15}BO_3$)	78·1	4·5	17·4			
CLXIV ($C_{22}H_{13}BO_2$)	82·5	4·1	13·4	83·1	4·4	12·5

Table IX

This was again suggested by the isolation of boric acid crystals during the working up of the hydroxyl derivative CLXXIII after this had been

treated with NaOH, and extracted with ether to separate boric acid (which is only slightly soluble in ether) and showed that the borate had been incompletely removed. Confirmation of the presence of boron was obtained by testing a small quantity of the product with p-nitrobenzene-azo-chromotropic acid reagent, which developed a blue colour as it does in the presence of a borate.[229]

The presence of a borate explains the peculiar behaviour after melting of the compound melting at 199-202°C., as the orthoboric ester (CLXIII) would be expected to lose water on heating to form the metaboric ester (CLXIV) by analogy with orthoboric acid which loses water at 100°C. to form metaboric acid.



CLXIII CLXIV

The failure of the mixed melting-point to show a depression is also explained. It is of interest to note that the borate would appear to have protected the hydroxyl group from the palladium catalyst which would be expected to remove a hydroxyl group.

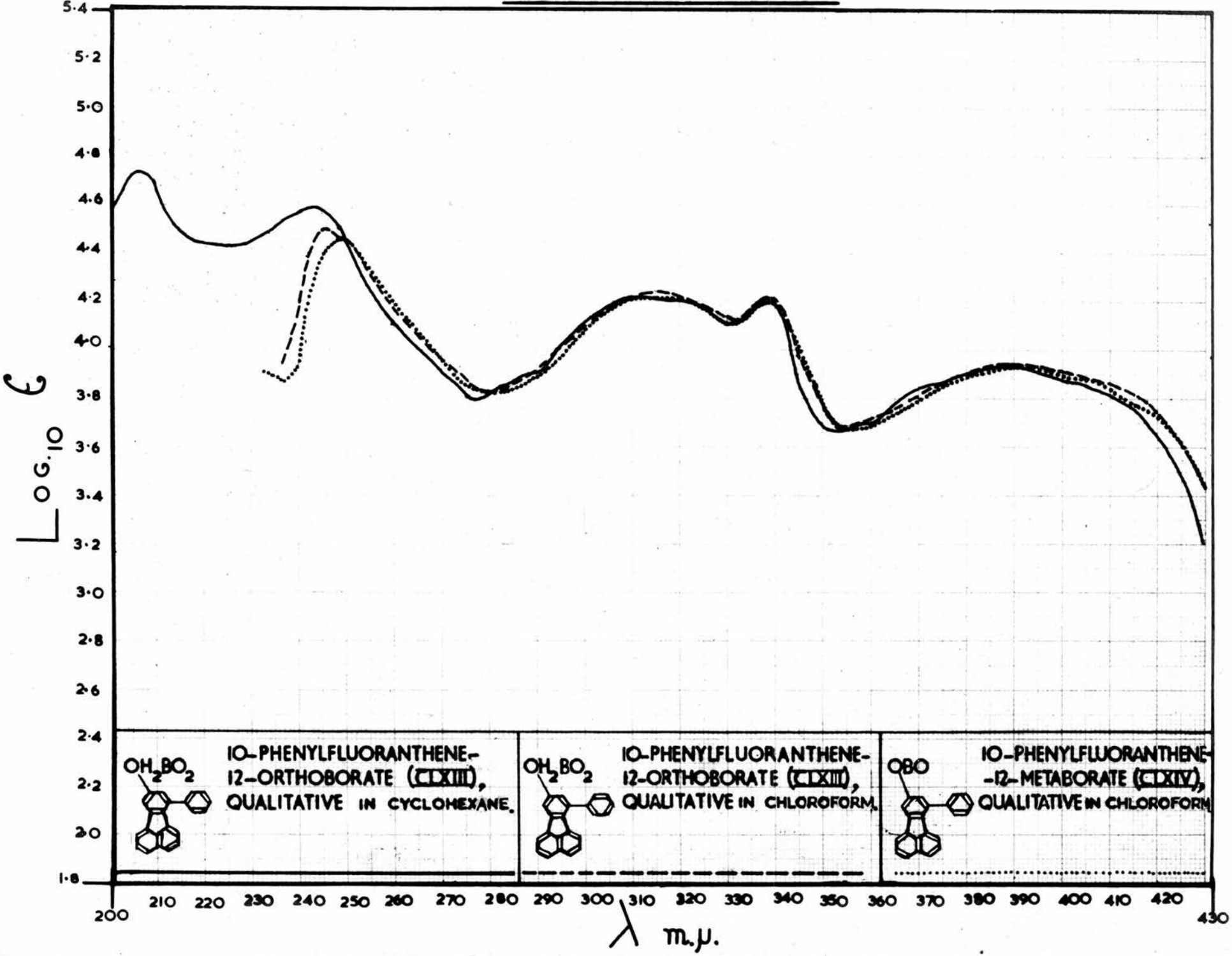
Although no 10-phenylfluoranthene (VII) was isolated during this work, and lack of time prevented repetition of the final stages, it would seem likely that a synthesis of this compound is available by the method shown in Scheme S, p. 110.

The series of reactions subsequent on the condensation of 7-benzylideneacenaphthene-8-one (IV) with acetoacetic ester (CLI) has now been discussed, but before describing condensation of 7-benzylideneacenaphthene-8-one (IV) with α:γ-diphenylacetoacetic ester (CLXXXI), the properties of the two compounds which were obtained from acetoacetic ester and 7-benzylideneacenaphthene-8-one, believed to be 10-phenyl-11-carbethoxytetrahydrofluoranthene-12-ones LXV and CLVI, will be discussed in more detail.

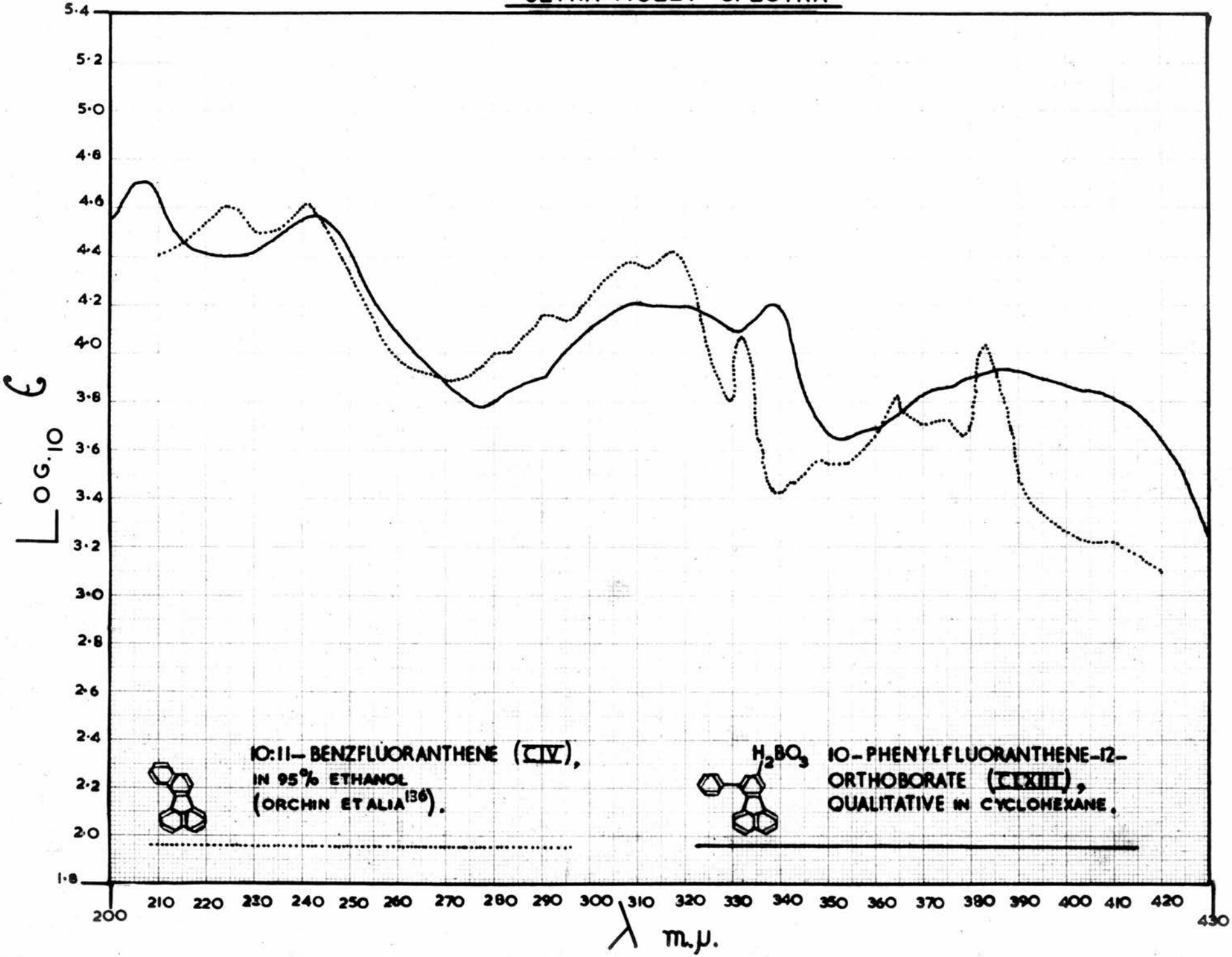
The synthesis of the compounds believed to be LXV and CLVI was unambiguous, and would be expected to form CLV, from which CLVI could arise by removal of water, and analysis of the compound melting at 180-181·5°C. showed it to correspond in composition with the ring-closed compound CLVI. The analysis of the compound melting at 160-2°C., which was only formed in relatively small quantities, lay between the compositions of CLV and CLVI (Table VII, p. 111).

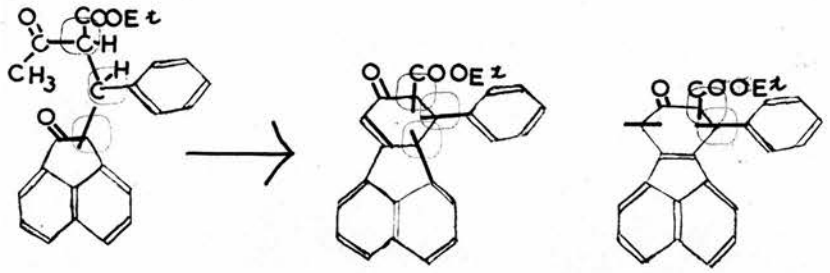
The ultra-violet spectrum (p. 45) of the compound melting at 180-181·5°C. shows a strong resemblance to the spectrum of 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII, see p. 43), the synthesis of which suggested its double bond to be acenaphthylenic,

ULTRA-VIOLET SPECTRA



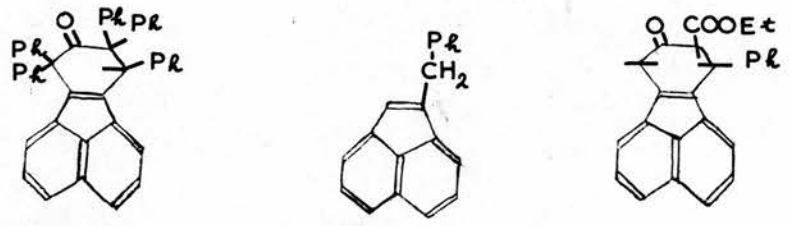
ULTRA-VIOLET SPECTRA





CLV CLVI LXV

and resembles to a lesser degree the spectrum of acenaphthylene (X), and the compound had the characteristic canary yellow colour associated with acenaphthylene derivatives. This suggested that the ring-closure had caused the formation of the acenaphthylenic compound LXV rather than the acenaphthenyl compound CLVI. An attempted Grignard reaction[39,49,240] to synthesise 7-benzylacenaphthylene (CXCIV) for spectroscopic comparison was unsuccessful.



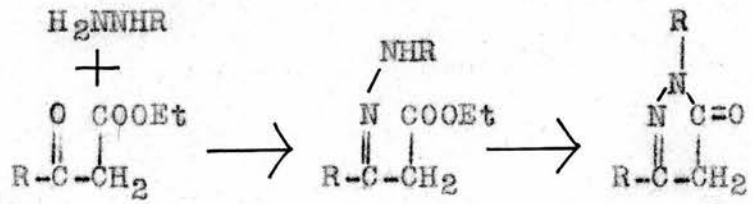
XLVIII CXCIV LXV

Confirmation of the structure LXV for this compound was obtained by the formation of a 2:4-dinitrophenylhydrazone by Allen's method[140], which showed the presence of the carbonyl group even though this could not be reduced by the Clemmensen or Wolff-Kishner methods[158-160,221,222]. The ultra-violet spectrum

p 226.

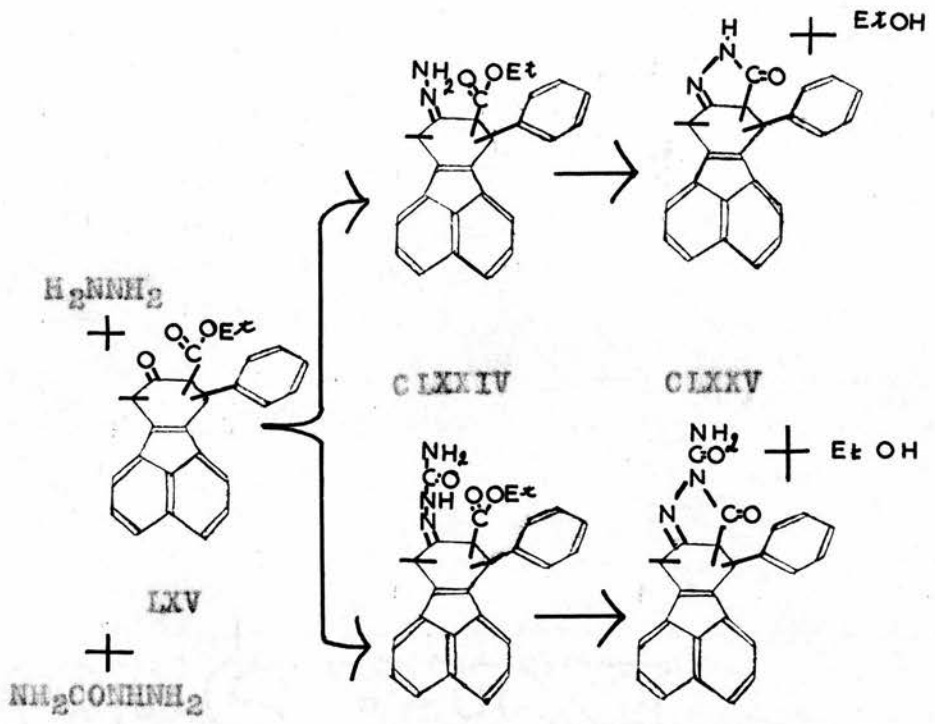
of the 2:4-dinitrophenylhydrazone is shown on p.256 along with that of the 2:4-dinitrophenylhydrazone of 7-benzylideneacenaphthene-8-one. Confirmation of the presence of the ester group was obtained by its removal on boiling under reflux with aqueous aceticacid containing sulphuric acid to form 10-phenyl-9:10:11:12-tetrahydrofluoranthene-12-one (CLVII) melting at 187-9°C.

The compound LXV is the ester of a β-ketonic acid and such compounds have been shown by Knorr[225] to react with hydrazines to form pyrazolone derivatives (see Scheme V), and the formation by the Wolff-Kishner reaction of nitrogenous products from both the hydrazone of LXV (CLXXIV) and the semicarbazone of LXV (CLXXVI) is therefore explained as these compounds were probably pyrazolone derivatives such as CLXXV and CXC. The bulk of the 2:4-dinitrophenyl substituent of the 2:4-dinitrophenylhydrazone of LXV would probably prevent, as is indicated by analysis, the formation of a pyrazolone from this (p.226).



Scheme V

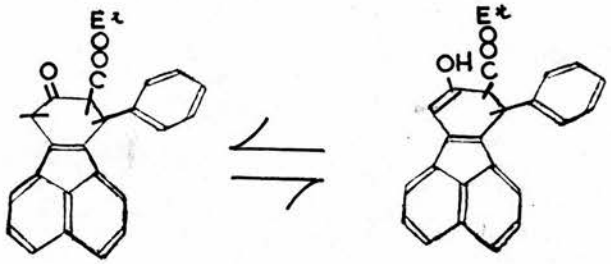
An attempt to confirm the presence of the acenaphthylenic double-bond in LXV by hydrogenation was unsuccessful, and decolourisation of bromine



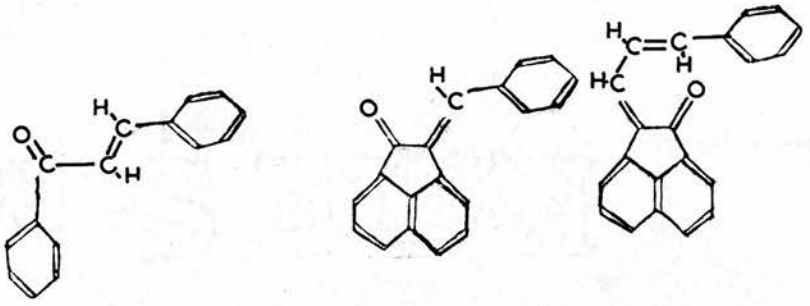
did not occur except extremely slowly, and it appears that this double-bond like that in 10:10:12:13:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11one (XLVIII) is rather inactive, probably for similar reasons (see p. 44).

The ethanolic solution of the compound melting at 180-181·5°C. was found to give a slight yellow colour with a tinge of violet when treated with ferric chloride solution, and it was assumed that enolisation to form 10-phenyl-11-carbethoxy-10:11-dihydrofluoranthene-12-ol (CLXVIII) must have occurred. To test this, the ultra-violet spectrum of a solution of the compound melting at 180-181·5°C. was observed in ethanol containing a small percentage of sodium as its ethoxide (variation from 0·025%

to 0·005% of sodium made little difference to this spectrum). This spectrum is shown on p. 161 along



LXV CLXVIII

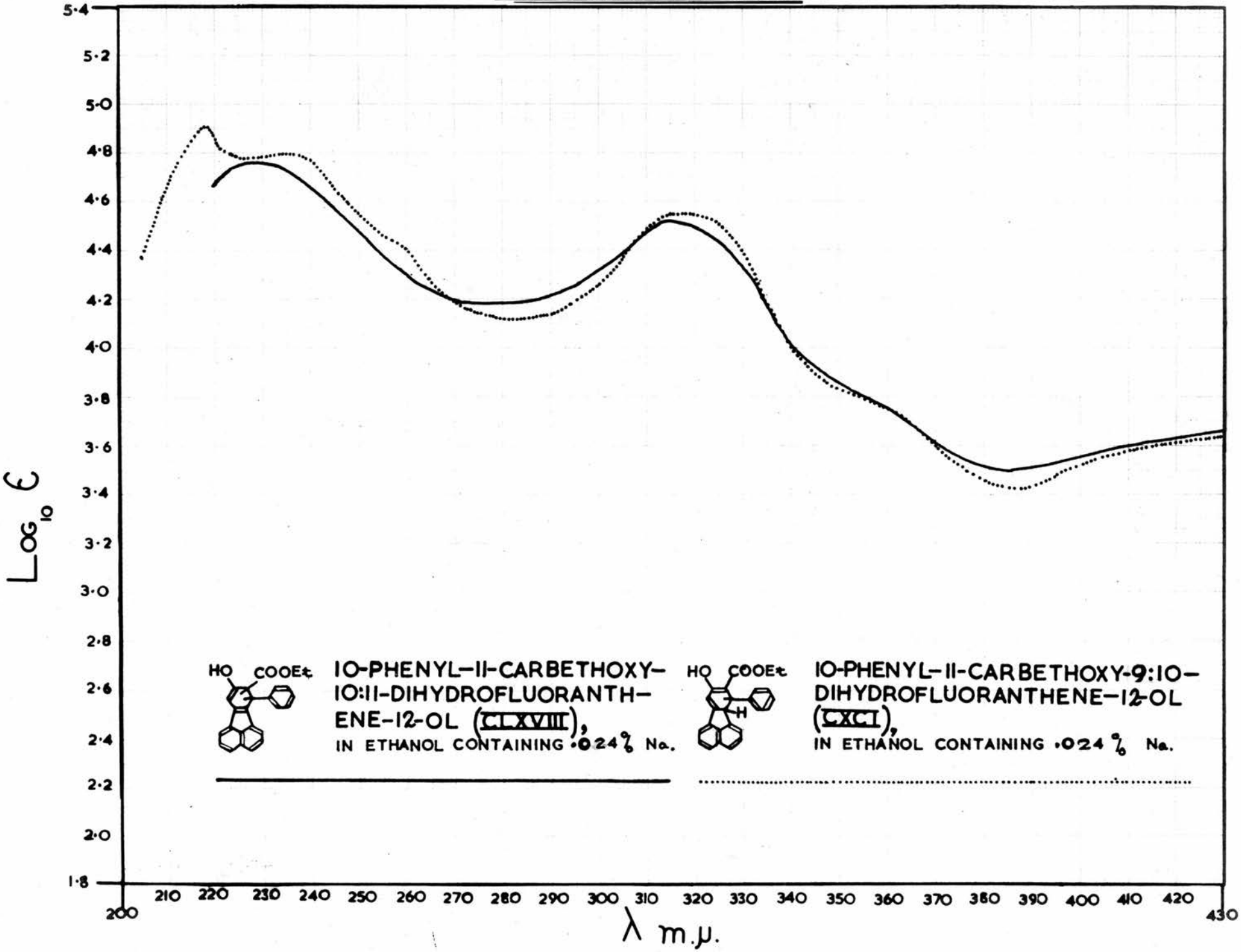


XVI IV CLXX

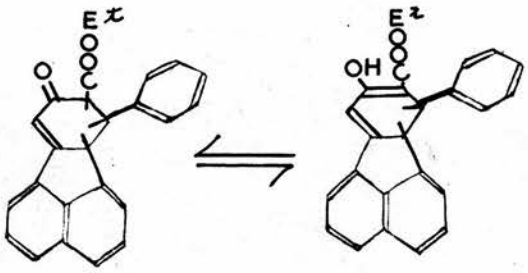
with the spectra of chalkone (XVI), 7-benzylidene-acenaphthene-8-one (IV) and 7-cinnamylideneacenaphthene-8-one (CLXX), and shows general resemblances to these which are probably caused by the existence in each compound of a conjugated pair of double-bonds.

The spectrum of the yellow compound, M.P. 180-181.5°C., in alkaline ethanol is very similar to the spectrum of the pale yellow compound, M.P. 160-2°C., in alkaline ethanol (p. 130), though the spectra in pure ethanol are quite different (p. 118). This result implies that the compounds formed on enolisation were closely similar in structure, and is explicable if the compound melting at 160-2°C. were 10-phenyl-11-carbethoxy-9:10:11:12-tetrahydro-

ULTRAVIOLET SPECTRA



fluoranthene-12-one (CLVI) and enolised to 10-phenyl-11-carbethoxy-9:10-dihydrofluoranthene-12-ol (CXCI), which would be expected to have a very

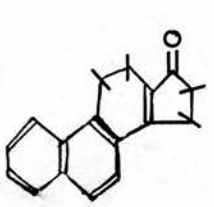


CLVI CXCI

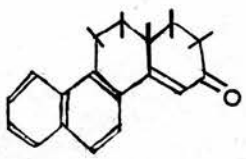
similar spectrum to that of 10-phenyl-11-carbethoxy-10:11-dihydrofluoranthene-12-ol (CLXVIII), the enolate of 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one (LXV, p.129). The development of a yellow orange colour with an ethanolic solution of the compound of M.P. 160-2°C. in the presence of ferric chloride solution confirmed that enolisation was occurring.

The compound CLVI is an α:β-unsaturated ketone and the ultra-violet spectrum of the compound of M.P. 160-2°C. shows some resemblances to those of the α:β-unsaturated ketones 7-benzylideneacenaphthene-8-one (IV) and 3'-keto-3:4-dihydro-1:2-cyclopentenophenanthrene[236] (CLXXXVII) especially in that it has the multipeaked form of the latter with roughly corresponding peaks A-C (p.134). It also more closely resembles its spectrum in alkaline ethanol than does the spectrum of the compound melting at 180-181.5°C., but this would be expected as the acenaphthylenic double-bond in LXV is not

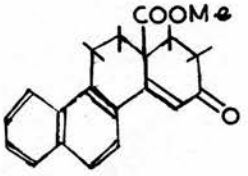
conjugated with the carbonyl double-bond except when it is enolised, while conjugation exists for both the keto and enol forms of CLVI (ps. 129 & 131). It should be noted from the similarity of



CLXXXVII



CLXXXVIII



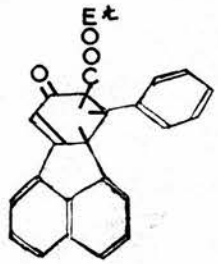
CLXXXIX

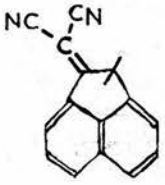
the spectra of 3-keto-1:2:3:11:12:12a-hexahydrochrysene (CLXXXVIII) and 3-keto-12a-carbomethoxy-1:2:3:11:12:12a hexahydrochrysene (CLXXXIX) that the presence of the ester group is unlikely to effect these comparisons[236] (p. 135).

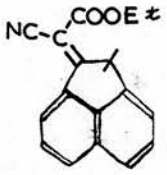
The α:β-unsaturated nature of the ketonic grouping was confirmed by the fact that the compound melting at 160-2°C. would not form a 2:4-dinitrophenylhydrazone by Brady's method[139,156] (it should be noted that an attempt to prepare the 2:4-dinitrophenylhydrazone of LXV by Brady's method was also unsuccessful, see p. 226), and by its failure to decolourise bromine, while it was only eluted with difficulty from an alumina column. A fresh solution of 1% of conc. HCl in dry acetone was found to be useful for removing this and other substances that attached themselves firmly to alumina, as it dissolves very little alumina.

Compound CLVI contains an acenaphthenylic double-bond and, in order to obtain further spectroscopic evidence, acenaphthenylmalonitrile[214,237,241] (CXCII)

and acenaphthenylcyanoacetic ester (CXCIII) were prepared as both these contain the same kind of double-bond. Only the latter compound was stable enough to give a reliable spectrum, and this more



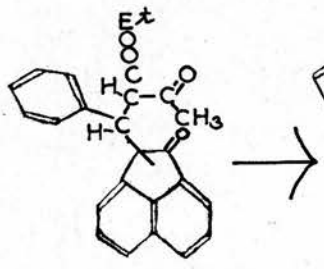


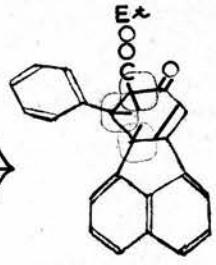


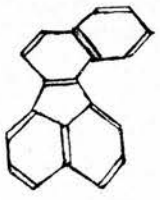
CLVI CXCII CXCIII

closely resembled the spectrum of the compound melting at 160-2°C. than that of the compound melting at 180-181·5°C. (p.136).

The analysis of the compound melting at 160-2°C. lay between the theoretical analyses of CLV and CLVI (p. 111), but the spectrum of this compound was found to show a strong resemblance to that of 10:11-benzfluoranthene (CIV), which showed that the compound was a fluoranthene derivative and therefore could not be CLV. It is more difficult to



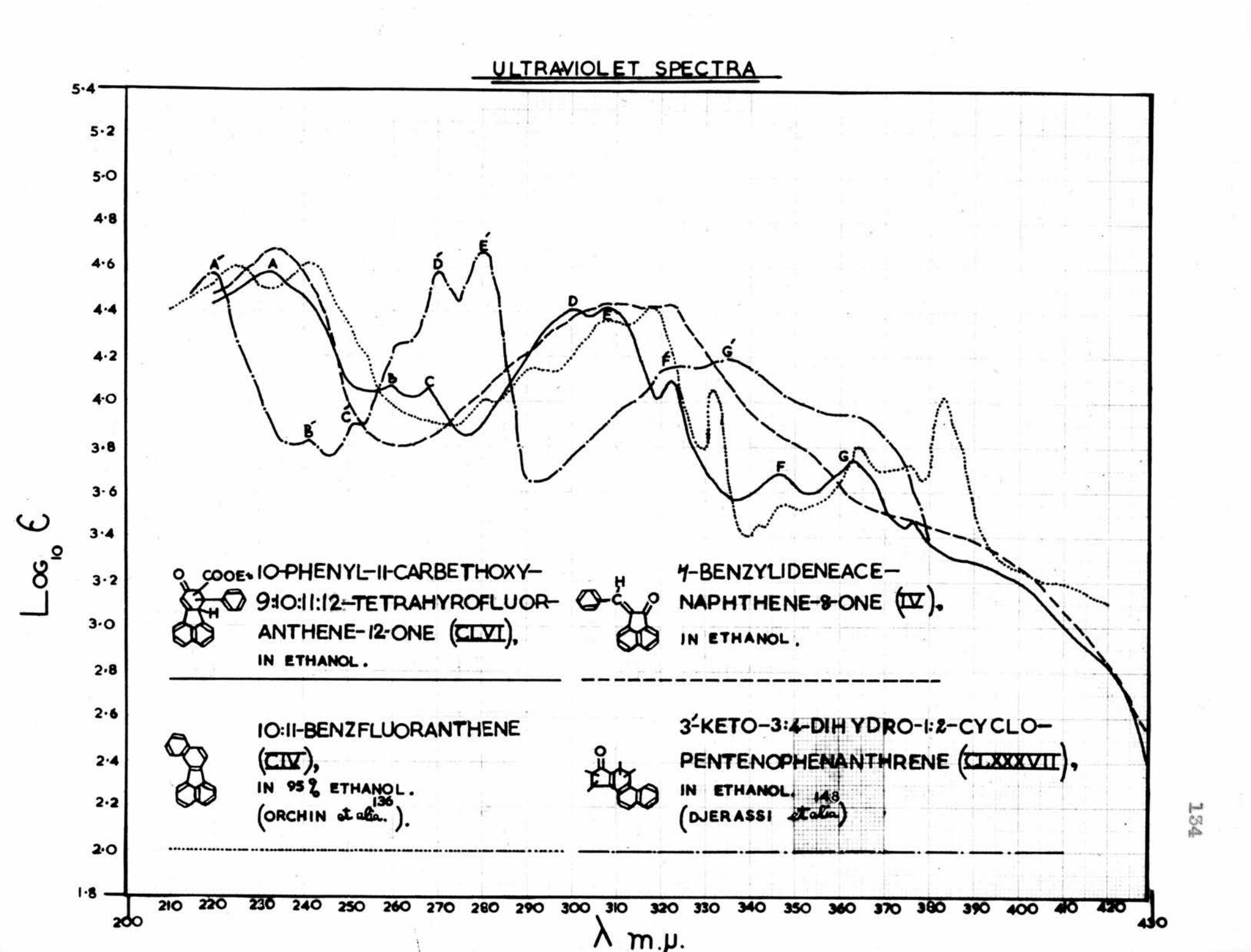




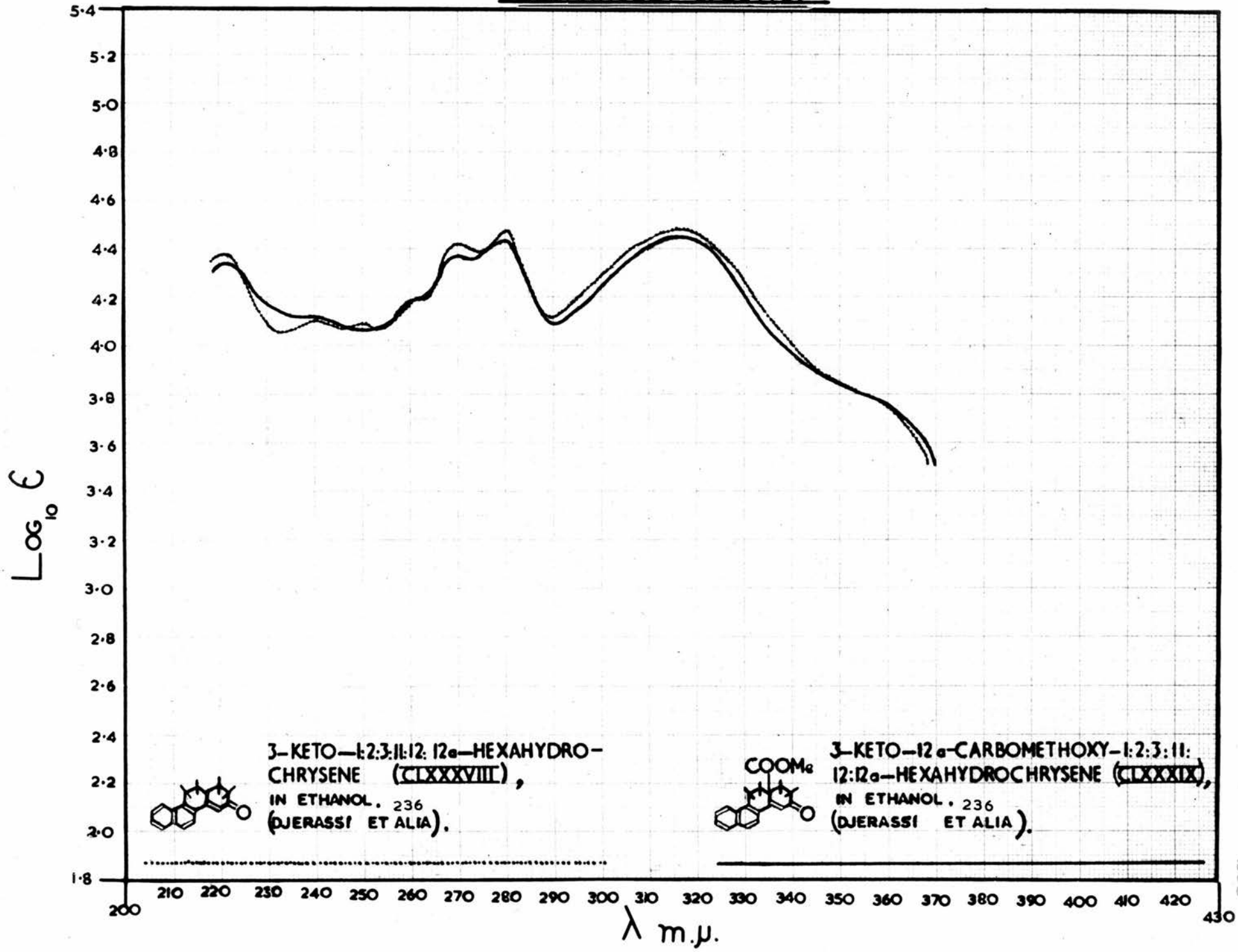
CLV CLVI CIV

explain this close similarity of the spectra of a tetrahydrofluoranthene and a fully aromatic fluoranthene, though this may be caused by the

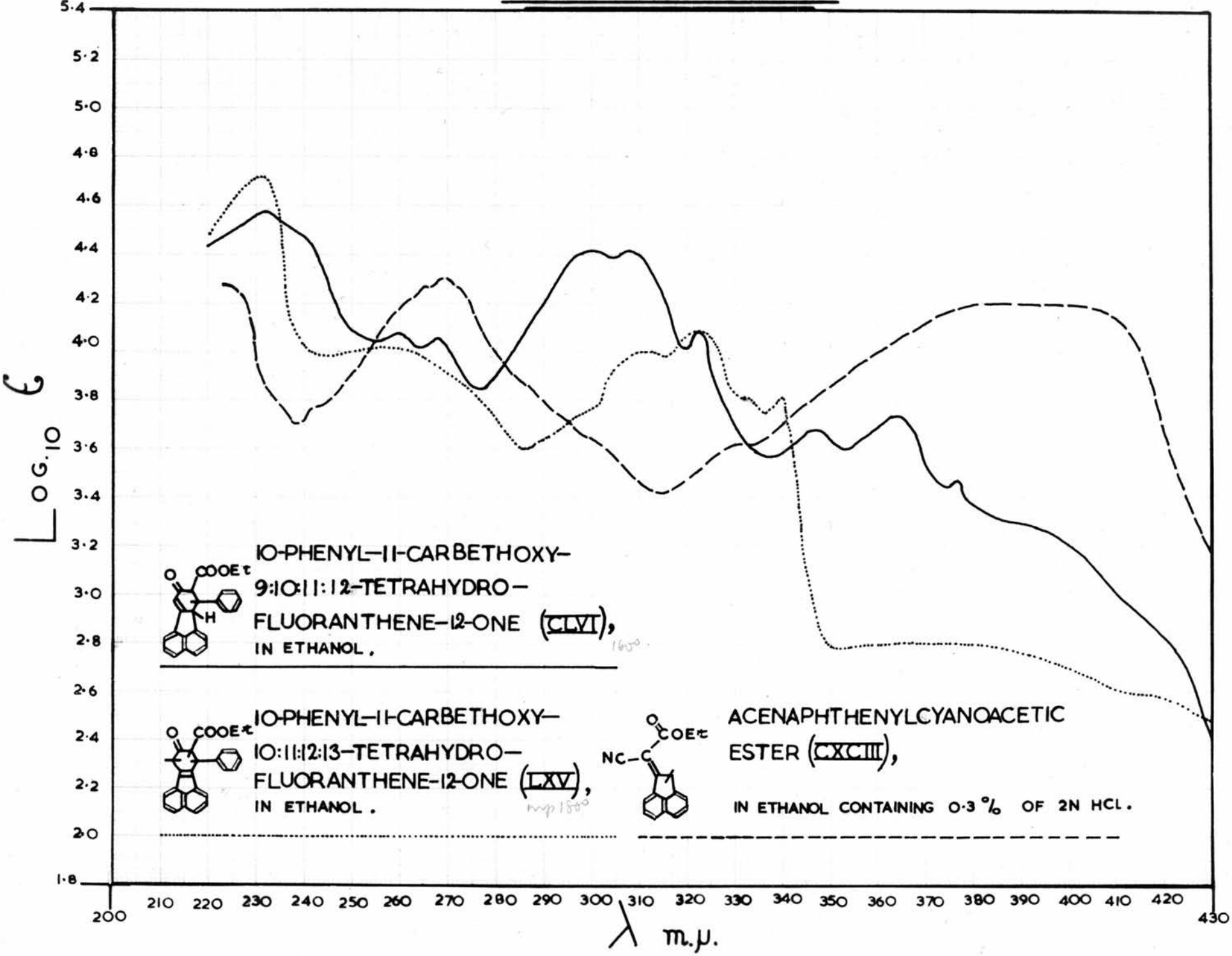
ULTRAVIOLET SPECTRA



ULTRAVIOLET SPECTRA



ULTRA-VIOLET SPECTRA

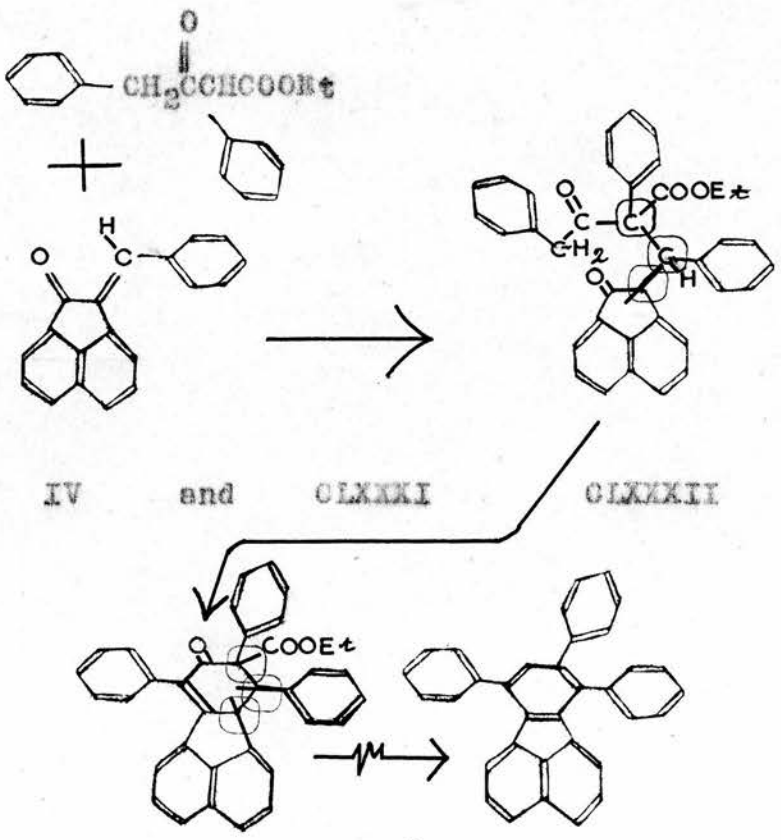


conjugated ketonic and ethylenic double-bonds of the former.

In conclusion, compound CLVI is the most likely product of the condensation of acetoacetic ester and 7-benzylideneacenaphthene-8-one, and though the three asymmetric carbon atoms this contains would be expected to give rise to isomers the differences between these would not be sufficient to explain the differences between the spectra of the two reaction products believed to be LXV and CLVI (p. 118). As the structure of the compound melting at 180-181.5°C. seems beyond reasonable doubt to be 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one (LXV), the compound melting at 160-2°C. would seem likely from the course of the formative reaction, and on balance from its properties, to be 10-phenyl-11-carbethoxy-9:10:11:12-tetrahydroflouranthene-12-one (CLVI).

Condensation of 7-Benzylideneacenaphthene-8-one with α:γ-Diphenylacetoacetic Ester

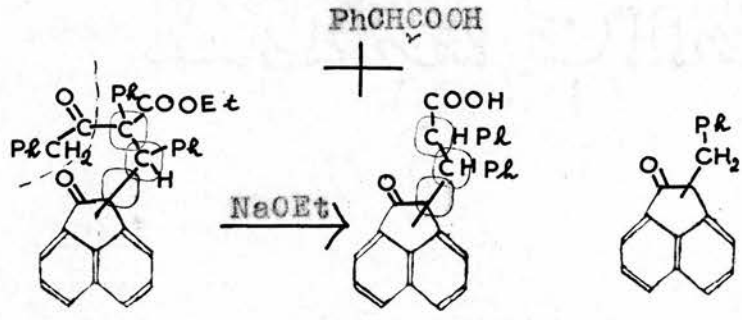
Since 7-benzylideneacenaphthene-8-one (IV) readily condensed with acetoacetic ester, CLI, (p. 109), it was decided to carry out an exploratory condensation between 7-benzylideneacenaphthene-8-one (IV) and α:γ-diphenylacetoacetic ester (CLXXXI), with the intention of producing 10:11:13-triphenyl-11-carbethoxy-9:10:11:12-tetrahydrofluoranthene-12-one (CLXXXIII) which it was hoped might eventually be converted into 10:11:13-triphenylfluoranthene[89] (CLXXXIV), see Scheme U.



Scheme U

The condensation was carried out by the Michael method[215] using a monomolecular proportion of sodium in ethanol as catalyst. A good yield of a mixture of two compounds was obtained, which was separated with some difficulty into its constituents, one forming monoclinic crystals of M.P. 202-3°C., and the other tetragonal crystals of M.P. 247-250°C.

The analyses of these compounds did not accord well with the theoretical analyses of either CLXXXII or CLXXXIII, but were fairly close to that of the unring-closed compound CLXXXII, suggesting that both compounds were isomers of this. As CLXXXII is a substituted acetoacetic ester, it might in theory undergo hydrolysis to the acid CLXXXV in the presence of sodium ethoxide, but as neither product was soluble in sodium carbonate solution, this is not likely. It is noteworthy



CLXXXII CLXXXV CXCVIII

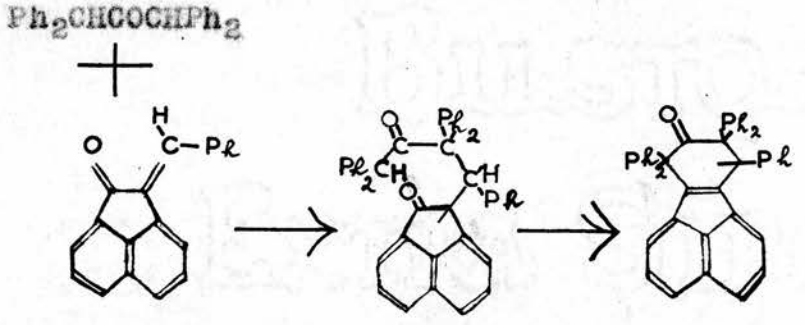
that 7-benzylacenaphthene-8-one (CXCVIII) is known to be colourless (p.252), and both CLXXXII and CLXXXV would therefore be expected to be colourless, as were both the reaction products, while the ring-

closed compound CLXXXIII would be expected from comparison with the acetoacetic ester derivatives LXV and CLVI to be yellow (p.109).

The indefinite result of the analyses, combined with the existence of three asymmetric carbon atoms in each of the likely products (shown emboxed) none of which could be readily removed without dehydrogenation and which gave rise to various possibilities of isomerism, suggested that further pursuit of this series of reactions was likely to be excessively involved, and the work was therefore discontinued.

Condensation of 7-Benzylideneacenaphthene-8-one with sym-Tetraphenylacetone

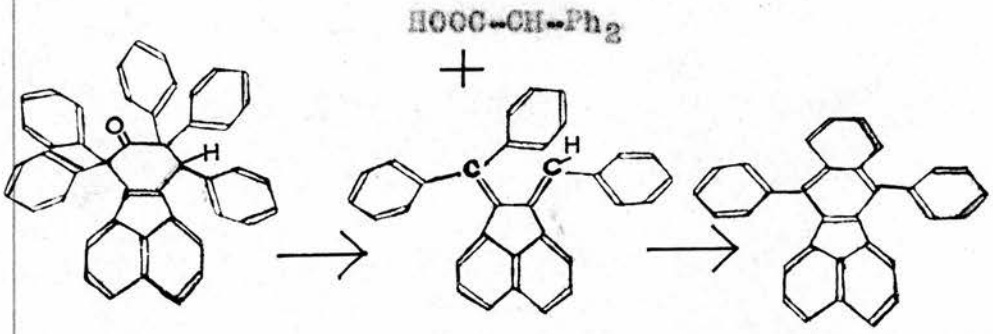
In view of the earlier synthesis of 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII, see p. 43) and the ready condensation of 7-benzylideneacenaphthene-8-one (IV) with acetoacetic ester (CLI, p. 109) and α:γ-diphenylacetoacetic ester (CLXXXI, p. 138), it seemed possible that 7-benzylideneacenaphthene-8-one (IV) would condense with sym-tetraphenylacetone (LXXVII) to form 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII).



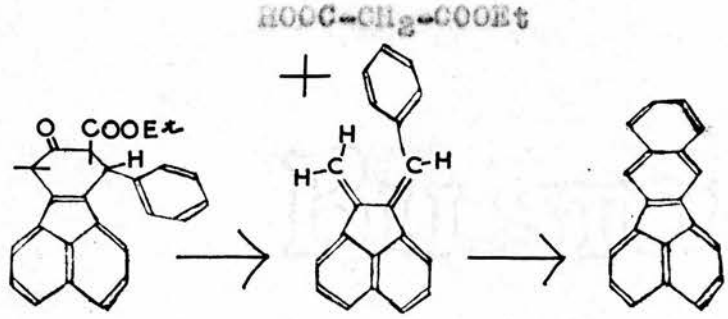
IV and LXXVII CC XLVIII

From the work with acetoacetic ester (CLI) and IV, the catalyst that seemed most likely to cause this reaction was sodium ethoxide. This is alkaline, and it has been shown (p. 182) that XLVIII is decomposed by alkali to form diphenylacetic acid (LXXVI) and 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII), the latter spontaneously ring-closing to form 10:13-diphenyl-11:12-benzfluoranth-

ene (LXIV). It was therefore hoped that if 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII) itself could not be isolated, its decomposition products would be obtained.



XLVIII LXXVI and XXXII LXIV



LXV CCIII LXII

The condensation was tried, using an excess of 7-benzylideneacenaphthene-8-one (IV) and, as catalyst, a monomolecular proportion of sodium in ethanol (Michael reaction)[215], and led to the isolation of both 10:13-diphenyl-11:12-benzfluoranthene (LXIV) and diphenylacetic acid (LXXVI), these being identified by mixed melting-point. An attempt to avoid the alkaline decomposition of XLVIII by repetition of the condensation using only catalytic quantities of sodium ethoxide (Kohler's method)[209] and a small

quantity of piperidine (Knoevenagel's method) as catalysts yielded a fluorescent solution which probably contained a small quantity of 10:13-diphenyl-11:12-benzfluoranthene (LXIV). Most of the starting material was recovered from this reaction, suggesting that the catalysts employed had not been adequate. No other pure substance was isolated from either reaction.

These reactions provided a further synthesis of 10:13-diphenyl-11:12-benzfluoranthene (LXIV) and, at the same time, indirect confirmation of the structure of the ketone XLVIII formed by the interaction of diphenylketene (XLII) and 7-benzylideneacenaphthene-8-one, IV, (p. 43).

Summary of Section IV

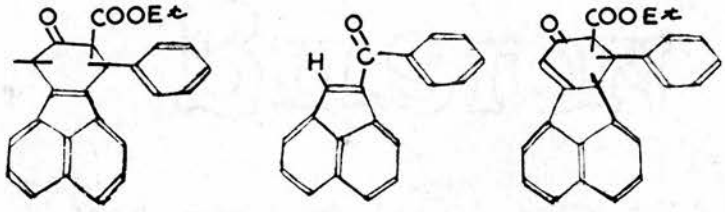
In conclusion, it has been shown that 7-benzylideneacenaphthene-8-one reacts readily with acetoacetic ester and its congeners to give condensates from which fluoranthene derivatives can be obtained. Where it is possible for isomerisation to occur, as with the condensates of acetoacetic ester and especially α:γ-diphenylacetoacetic ester, this was found to be troublesome, and the synthetic possibilities of neither reaction were exhausted.

Alkali has been shown to decompose 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII) to form 10:13-diphenyl-11:12-benzfluoranthene (LXIV), and an experiment with a small quantity of 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one (LXV) showed this also to decompose when treated with alkali, though no product was isolated. It is noteworthy that if these reactions were analogous, despite the lack of a diphenylmethylene group in CCIII, 11:12-benzfluoranthene (LXII) might be produced from the latter.

Section V

The Preparation and Properties of the Ketochloride of 7-Benzylideneacenaphthene-8-one

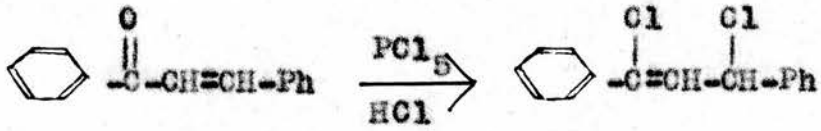
The original intention of this research was to utilise the chalkone like properties of 7-benzylideneacenaphthene-8-one (IV) to synthesise 7-benzoylacenaphthylene (CCIV), as in Scheme Y, for spectroscopic comparison with the 10-phenyl-11-carbethoxytetrahydrofluoranthene-12-ones LXV and CLVI.



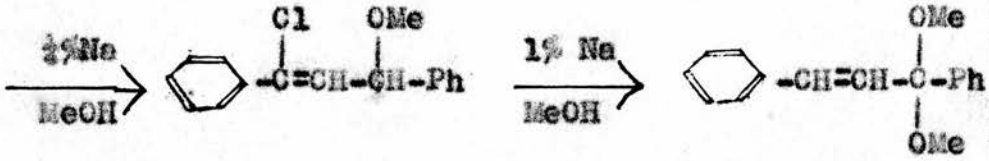
LXV 230,232 CCIV 234 CLVI

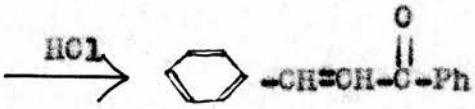
Straus and Staudinger have shown that some compounds containing a chalkone grouping, such as cinnamylideneacetophenone (CCV) and chalkone (XVI) itself, yield "ketochlorides" (CCVI and CCVII) when treated with PCl_5 and dry hydrogen chloride. These chalkones, when treated with PCl_5 and HCl followed by methylation and hydrolysis, undergo a permanent shift in the position of the double-bond and the carbonyl group, as in Scheme X.

It was therefore hoped that 7-benzylideneacenaphthene-8-one (IV) would undergo a similar bond

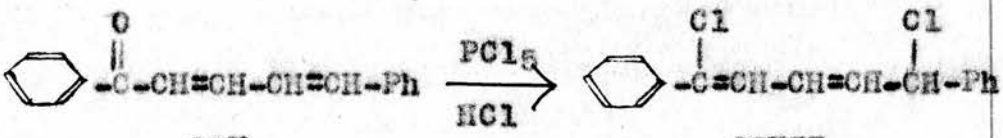


XVI CCVI

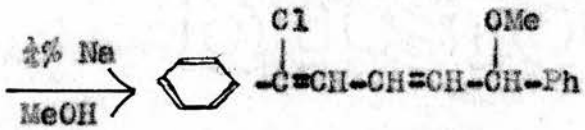


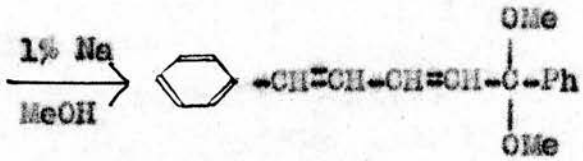


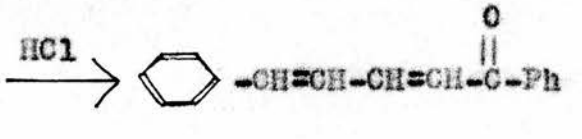
XVI



CCV CCVII



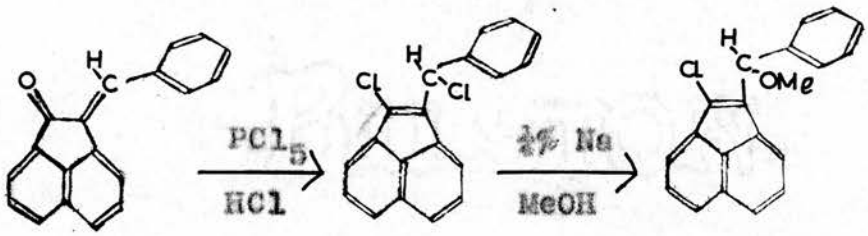




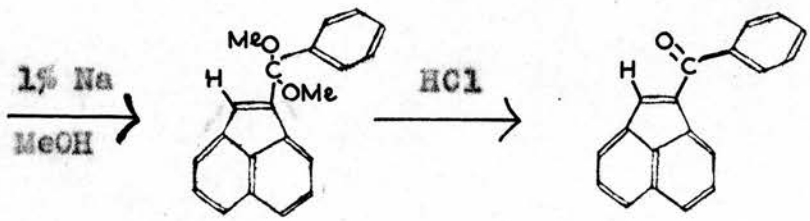
CCV

Scheme X

shift, as in Scheme Y, to form 7-benzoylacenaphthylene (CCIV). The series of reactions was tried, using Straus's[230,232] method on 7-benzylideneacenaphthene-8-one (IV), but it was found that the second methylation could not be effected, though the ketochloride CCVIII (M.P. 72°C.) and its monomethoxy derivative LXIX (M.P. 60-61·5°C.) were isolated. Hydrolysis of the monomethoxy compound LXIX yielded the starting material, 7-benzylideneacenaphthene-8-one (IV), instead of the expected 7-benzoylacenaphthylene (CCIV), and the reaction was therefore assumed to have taken the course shown in Scheme Z.



IV CCVIII LXIX

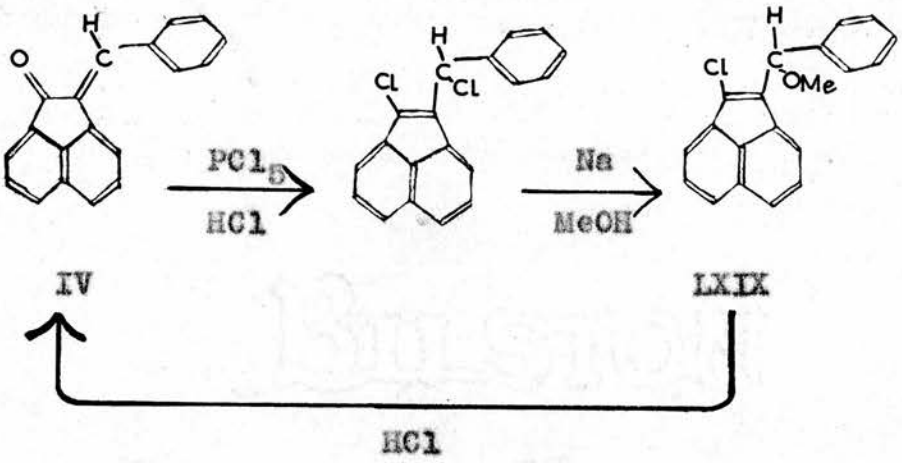


CCIV

Scheme Y

Structures were assigned to the products obtained from 7-benzylideneacenaphthene-8-one (IV) by analogy with those of the chalkone derivatives in Scheme X, and in the case of the ketochloride CCVIII

and the monomethoxy derivative LXIX, the structures were confirmed by analysis. The ultra-violet spectrum of the latter (LXIX) was observed and found to be almost identical with that of acenaphthylene (X, see p. 69), showing the compound to be an acenaphthylene derivative. The hydrolysis of LXIX to 7-benzylideneacenaphthene-8-one (IV) was proved by a mixed melting-point determination with a specimen of IV.



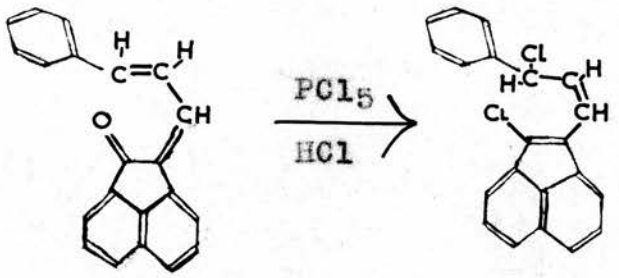
Scheme Z

Attempts to methylate the second chlorine atom in LXIX were made using 1%, 2% and 10% sodium in methanol, and 2% potassium in methanol, with up to 60 hour periods of reflux, but only unchanged starting material LXIX was isolated from these reactions.

In view of the failure to obtain the expected series of reactions, the techniques used were tested by carrying through the whole cycle of reactions shown in Scheme X (p. 146) with both chalkone (XVI) and cinnamylideneacetophenone (CCV), and in both

cases the results accorded with those of the earlier workers.

Since the reaction techniques had proved satisfactory, 7-cinnamylideneacenaphthene-8-one (CLXX) was prepared and treated with PCl_5 and HCl, but its ketochloride (CCIX), which was shown by colour reactions to be present in solution, could not be isolated as a solid. Ketochlorides are difficult



CLXX CCIX

compounds to handle, as they are extremely sensitive to moisture and thus must be preserved from contact with air, and since in spite of all precautions no crystalline product was isolated from this reaction, it was not pursued further.

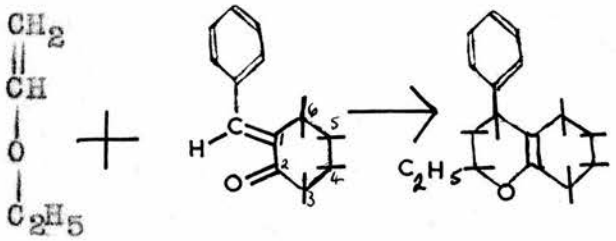
In conclusion, this work shows that 7-benzylideneacenaphthene-8-one (IV) differs from the simpler chalkones in that preparation, methylation and hydrolysis of its ketochloride does not produce the shift of the position of the double-bond and the carbonyl group that would be expected by analogy with the simpler chalkones.

Section VI

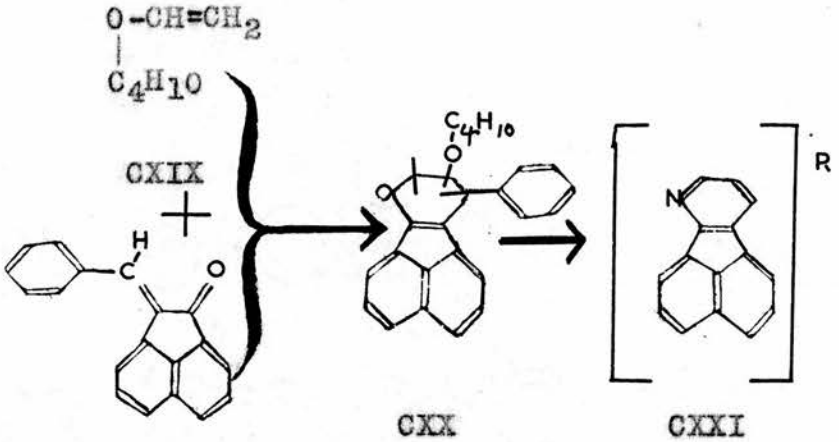
Attempted Diene Reactions with 7-Benzylideneacenaphthene-8-one and Diene Reactions with some other Chalkones

This section comprises attempted diene reactions between 7-benzylideneacenaphthene-8-one and vinyl butyl ether, diphenylketene and acetylene, and comments on the reaction with phenylketene. The descriptions of a reaction between vinyl butyl ether and cyclohexanone under mild conditions, and of the effect of ketene and diphenylketene on chalkone are included.

It has been shown by Emerson, Birum and Longley[175] and by F.G. Young[176] that α:β-unsaturated ketones can behave as dienes and undergo diene reactions to form pyran derivatives, and it was hoped that by the use of these reactions oxafluoranthene derivatives, and hence azafluoranthene derivatives, might be produced. The former workers[175] showed that by heating ethyl vinyl ether (CXVI) with 1-benzylidenecyclohexane-2-one (CXVII)[177] in a sealed tube, 2-ethoxy-3:4:5:6:7:8-hexahydro-4-phenyl-2H-benzopyran (CXVIII) was produced (Scheme Q), and that similar compounds could be produced from other α:β-unsaturated ketones.



CXVI CXVII CXVIII



CXIX

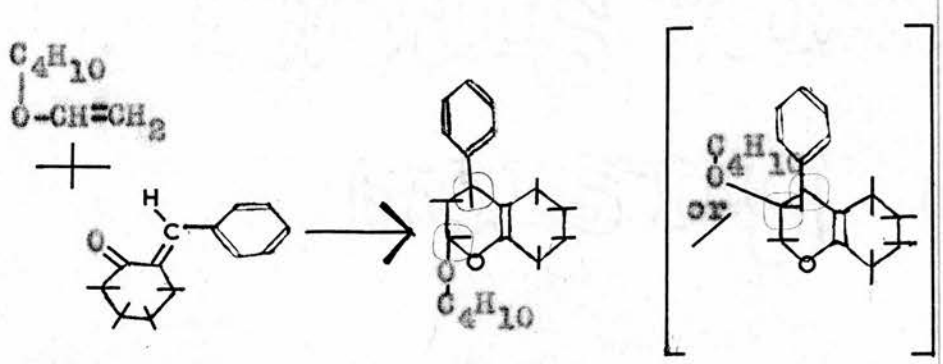
IV CXX CXXI

Scheme Q

Reactions were therefore tried by heating 7-benzylideneacenaphthene-8-one (IV) with vinyl butyl ether (CXIX) in a sealed Carius tube at both 190°C. and 225°C. for a period of 16 hours in the hope of obtaining 13-phenyl-11:12-dihydro-10-oxafluoranthene (CXX), from which it was hoped a derivative of 10-azafluoranthene (CXXI) might be formed. Both reactions gave tars which on careful working up yielded no pure product other than unchanged IV.

It was felt that the reason for failure was that the reaction conditions were too vigorous, and the method was modified to allow the reaction to be carried out in the cold by adding a BF_3 catalyst to

the reaction mixture. The modified method was tried with butyl vinyl ether (CXVI) and 1-benzylideneecyclohexane-2-one (CXVII) and yielded a compound the physical properties of which closely resembled those of the 2-ethoxy-3:4:5:6:7:8-hexahydro-4-phenyl-2H-benzopyran (CXVIII) found by Emerson, Birum and Longley. The analysis of this compound suggested that it was the expected 2-butoxy-3:4:5:6:7:8-hexahydro-4-phenyl-2H-benzopyran (CXXII).



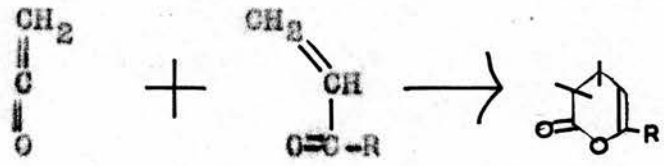
CXIX & CXVII CXXII CXXXI

This method of preparing a benzopyran is of interest as it eliminates the vigorous conditions used in Emerson, Birum and Longley's method and is therefore less likely than their method to cause unexpected structural changes in the reaction products.

A number of reactions were carried out by treating 7-benzylideneacenaphthene-8-one (IV) with butyl vinyl ether (CXIX) in the presence of BF_3 in the hope of obtaining the oxafluoranthene derivative (CXX), but here again the only product that was isolated was unchanged starting material, and it was concluded that 7-benzylideneacenaphthene-8-one

(IV) would not react with vinyl butyl ether (CXIX) in the same manner as the simpler α:β-unsaturated ketones.

Reference has already been made to the work of F.G. Young.[176] This investigator showed that ketene (CIX) can react with vinyl alkyl ketones (CXXIV) in the presence of BF_3 catalyst to form α-pyrones of the type 6-alkyl-3:4-dihydro-α-pyrone (CXXV).

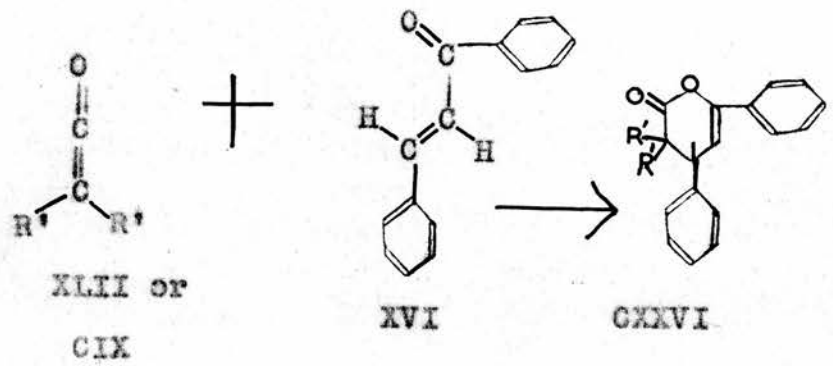


CIX CXXIV CXXV

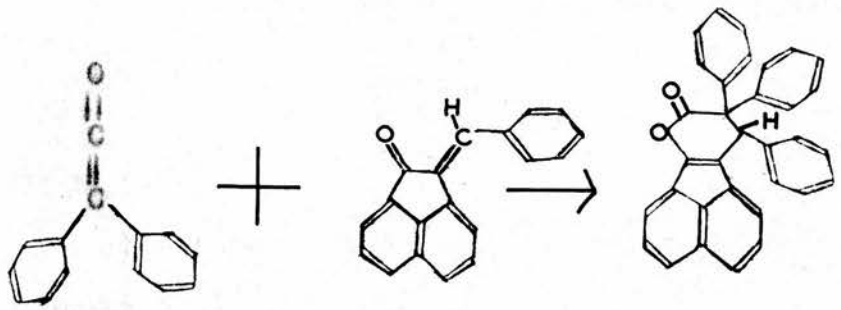
Reactions of this type were therefore tried with chalkone (XVI) using both ketene (CIX) and diphenylketene (XLII), and with 7-benzylideneacenaphthene-8-one (IV) using diphenylketene (XLII) in the hope of obtaining the products CXXVI and CXXIII respectively (Scheme R).

Only unchanged starting material and diphenylacetic acid were isolated from the reactions with diphenylketene, and it was concluded that this substance did not react with α:β-unsaturated ketones under the above conditions. In the case of the reaction between ketene (CIX) and chalkone (XVI), no pure product was isolated, but a bright red coloured product soluble in phosphoric acid was obtained in solution. The behaviour of this compound resembled the behaviour of the strongly coloured compounds produced by the action of phenylketene (CX) on chalkone (XVI) and 7-benzylideneacenaphthene-

8-one (IV), and the compound is referred to in connection with these (Part I, Section II, p. 96).



XLII or CIX XVI CXXVI



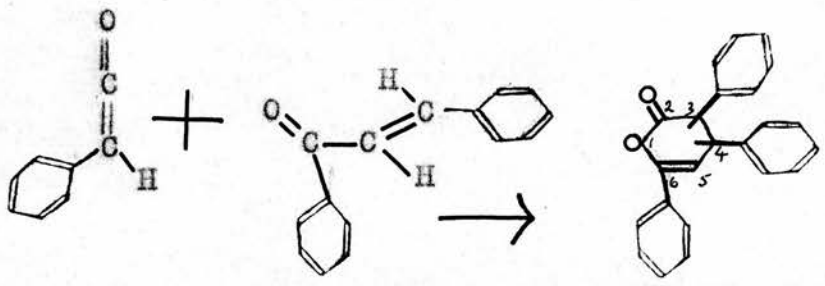
XLII IV CXXIII

Scheme R

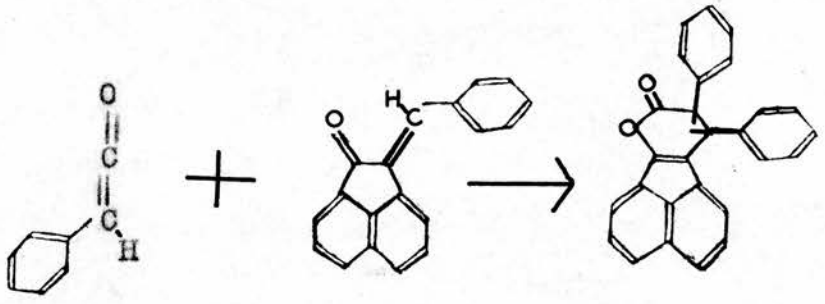
(R'= phenyl or hydrogen)

The solubility of these coloured compounds in phosphoric acid and the colour changes engendered by changes in pH would not be inconsistent with these compounds having pyrone structures, since substituted pyrones are often soluble in polar solvents, frequently form oxonium salts and are sometimes strongly coloured. The possible structures for the three red compounds, on the basis of Young's work, are shown below, and are 3:4:6-triphenyl-3:4-dihydro-α-pyrone (CXXVII), 3:4-diphenyl-5:6-perinaphthylene-3:4-dihydro-α-pyrone (CXXVIII) and 4:6-diphenyl-3:4-dihydro-α-pyrone (CXXIX),

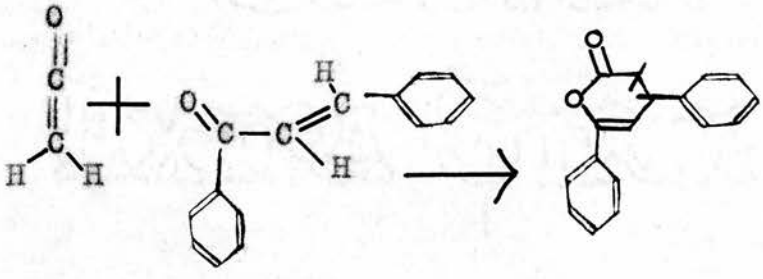
respectively, for the products of the interaction of phenylketene (CX) and chalkone (XVI), phenylketene (CX) and 7-benzylideneacenaphthene-8-one (IV), and ketene (CIX) and chalkone (XVI).



CX XVI CXXVII



CX IV CXXVIII



CIX XVI CXXIX

In each of these compounds the possibility of enolisation of the carbonyl exists, and this could account for part of the complex colour changes that the compounds displayed on change of pH, as well as accounting for the failure of diphenylketene (XLII) to form any corresponding strongly coloured product, as in this case the two phenyl substituents would prevent enolisation.

An unsuccessful exploratory attempt was also made to obtain a diene reaction between 7-benzylideneacenaphthene-8-one (IV)and acetylene in the presence of BF_3, but only unchanged starting material was obtained from this reaction.

In conclusion, diene reactions with vinyl butyl ether did not appear to occur so readily with 7-benzylideneacenaphthene-8-one as they do with alicyclic α:β-unsaturated ketones. Chalkone reacted with ketene in the presence of BF_3 to produce an intensely red product that was not isolated, but that appeared to be similar to the red products obtained by the interaction of phenylketene with chalkone and 7-benzylideneacenaphthene-8-one (p. 96).

Section VII

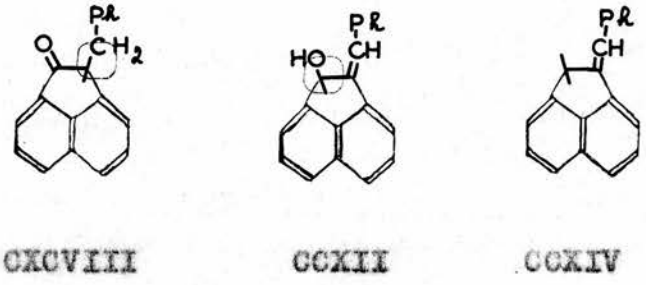
Some Reactions of 7-Benzylidene- and 7-(ortho-Bromobenzylidene)-acenaphthene-8-one

This section comprises a discussion of a number of experiments carried out to reduce 7-benzylideneacensphthene-8-one (IV) and a summary of the extent to which the compound behaves as an α:β-unsaturated ketone on the basis of all the work of this Thesis. The section is concluded with a short account of experiments carried out to form 7-(ortho-bromobenzylidene)-acenaphthene-8-one (CCX) and attempts to ring-close this to form 1:2-benz-4:5-ketomethylenephenanthrene (CCXI).

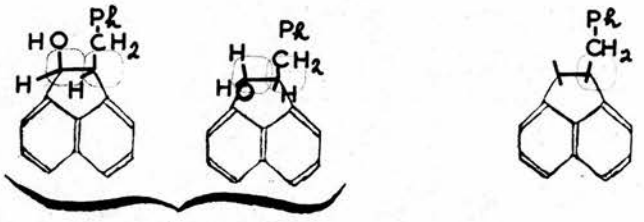
Reduction and Hydrogenation of 7-Benzylideneacenaphthene-8-one

Reduction and hydrogenation of 7-benzylidene-acenaphthene-8-one (IV) afforded uncrystallisable oils or poor yields of crystalline product. This is not entirely surprising when the number of simple reduction products theoretically obtainable is considered (Scheme AZ). Thus it was found that hydrogenation with Raney nickel as catalyst, and reductionsby the Clemmensen method, with zinc and sodium [158,159,160]

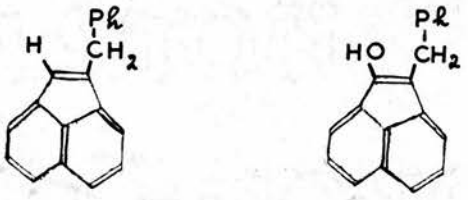
hydroxide or acetic acid, by the Meerwein-Ponndorf[254,246,256] method, with lithium aluminium hydride, by the Wolff-Kishner method,[250,278] and with red phosphorus and iodine[221,222] gave either no crystalline product, or only poor yields of crystalline product.[254] Hydrogenation



CXCVIII CCXII CCXIV



CCXIII CLXXXVI



CXCIV CCXV

Scheme A2

of IV with Raney nickel in the presence of hydrochloric acid, however, gave a good yield of 7-benzylacenaphthene-8-one (CXCVIII). This method was developed by Cornubert et alia[242,244,245] as a means of reducing the ethylenic double-bonds in α:β-unsaturated ketones.

The only reduction products that were isolated from these reactions and identified were: 7-benzyl-

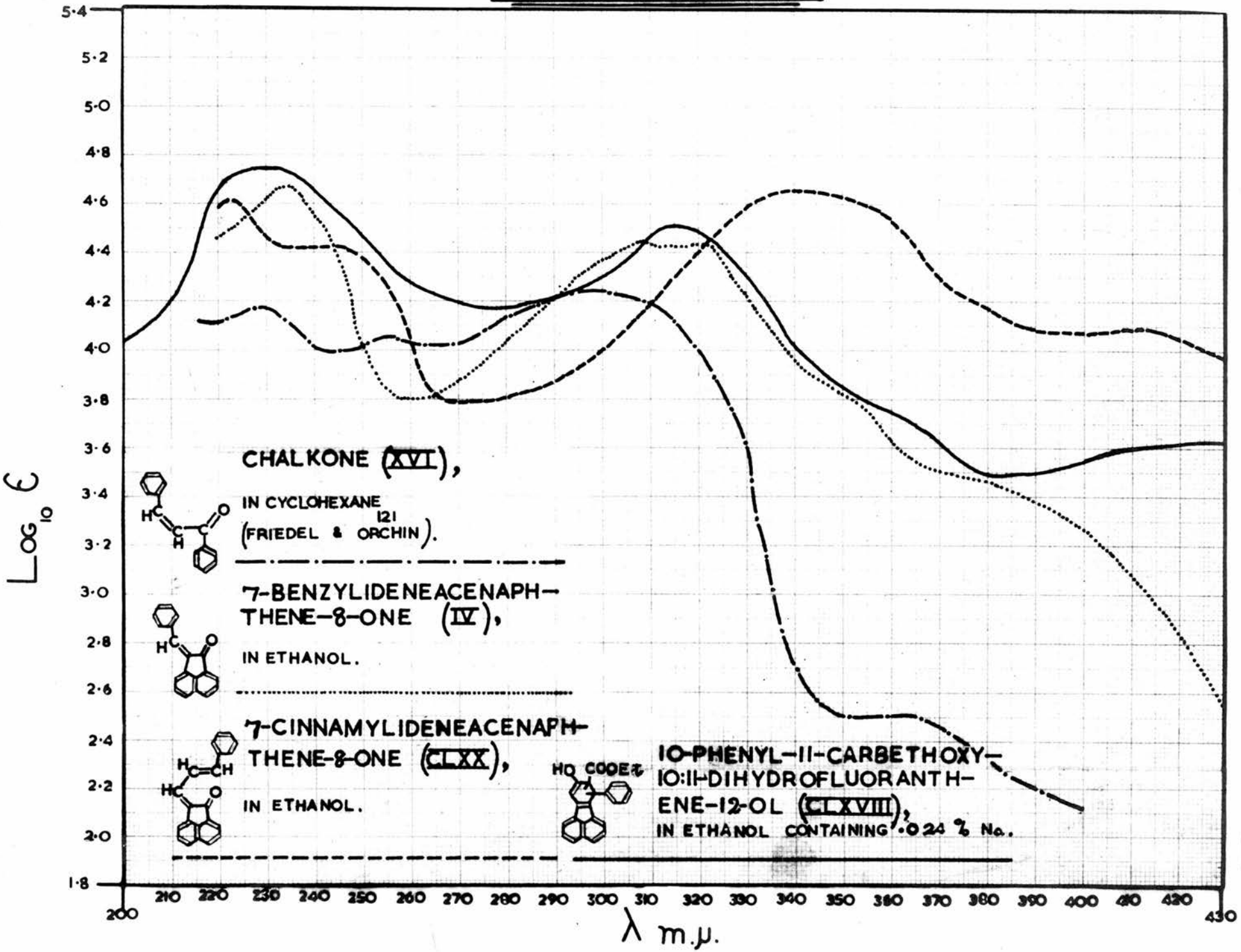
acenaphthene-8-one (CXCVIII, obtained from hydrogenations with Raney nickel in the presence of HCl[244] and with Adam's PtO_2 catalysts), 7-benzylideneacenaphthene (CCXIV, formed in poor yield by a Wolff-Kishner reduction[221,222]) and a small yield of a substance presumed to be 7-benzylideneacenaphthene-8-ol (CCXII, formed by a Meerwein-Ponndorf reduction[256]).

The α:β-Unsaturated Properties of 7-Benzylidene-acenaphthene-8-one

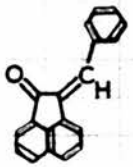
The difficulty of reducing and hydrogenating 7-benzylideneacenaphthene-8-one (IV), even with reducing agents which react specifically with either carbonyl of ethylenic groups, shows that the presence of the naphthalene system attached to the chalkone group of IV does not prevent conjugation and interaction of the ethylenic and carbonyl double-bonds. The α:β-unsaturated ketonic behaviour of 7-benzylideneacenaphthene-8-one (IV) was confirmed by the fact that the only reduction that gave nearly quantitative yields was one which is used specifically with α:β-unsaturated ketones (Cornubert[242,244], et alia[245]), while the ethylenic bond in IV only decolourised bromine in carbon tetrachloride solution very slowly. The carbonyl group did, however, form a 2:4-dinitrophenylhydrazone.

The ultra-violet spectrum of 7-benzylideneacenaphthene-8-one (IV) also shows the α:β-unsaturated nature of the compound as it is intermediate between the spectra of chalkone (XVI) and 7-cinnamylideneacenaphthene-8-one (CLXX) and resembles them in type (p. 161), but is quite different from the spectra of the ketones 7-benzylacenaphthene-8-one (CXCVIII), acenaphthene-8-one (III) and α-acetylnaphthalene (CCXVI) which closely resemble each

ULTRAVIOLET SPECTRA

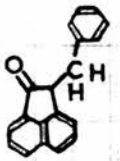


ULTRA-VIOLET SPECTRA



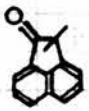
7-BENZYLIDENEACENAPHTHENE—8-ONE (IV),

IN ETHANOL.



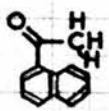
7-BENZYLACENAPHTHENE-8-ONE (CXCVIII),

IN ETHANOL.



ACENAPHTHENE-8-ONE (III),

IN ETHANOL BELOW 235 mμ.
IN CHOROFORM ABOVE 235 mμ.



α-ACETYLNAPHTHALENE (CCXVI),

IN ETHANOL.

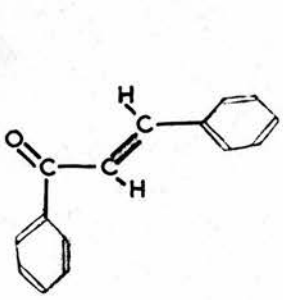
Log.10 ε

5·4 5·2 5·0 4·8 4·6 4·4 4·2 4·0 3·8 3·6 3·4 3·2 3·0 2·8 2·6 2·4 2·2 2·0 1·8

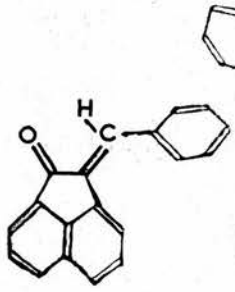
200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370 380 390 400 410 420 430

λ mμ.

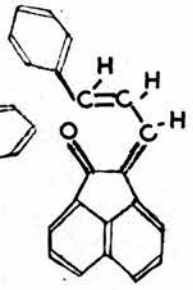
other (p. 162). The ultra-violet spectra of naphthalene and acenaphthene (VIII) are shown on p. 5 , and the curves on p. 162 show the influence of the ketonic group on these spectra, while those on p. 161 show the influence of the conjugated double-bond on the spectra of the ketones.



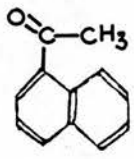
XVI



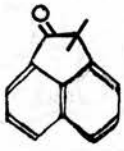
IV



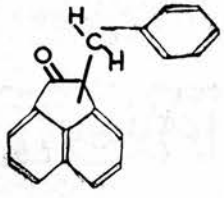
CLXX



CCXVI



III



CXCVIII

α:β-Unsaturated compounds, of which α:β-unsaturated ketones are only one example, are notable for their reactivity, and additions occur to this type of compound with: water and alcohols, ammonia[162,197] and amines, phenylhydrazines and piperazine, sulphides and mercaptans and thiophenols, Grignard[198][199][200,201][207,276] reagents, acetoacetic ester, malonic and other esters, cyclopentanone, other ketones and aldehydes, ketenes and ketene diethylacetal, vinyl butyl ether, phosphorus pentachloride and oxalyl chloride, and[208,209][210][211][212][271,272][123,124,176][213][175][230,232][206,234] and various other compounds such as nitrogen trichloride, nitromethane, hydrocyanic acid and nitriles.[202][203][193,204][194,205] During the work of this Thesis, a large

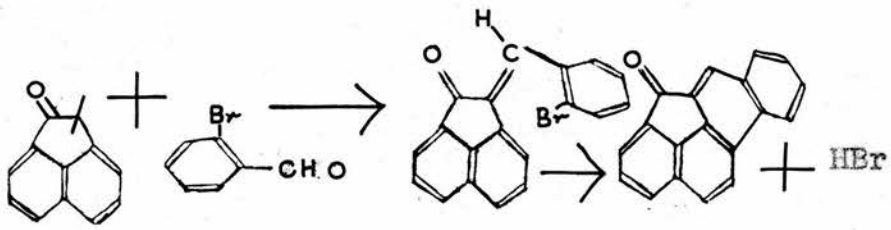
Reagent	Reaction or Product Expected	Reaction or Product Obtained	Section
2:4-Dinitrophenylhydrazine	Addition to 2:4-dinitrophenylhydrazone	Addition to 2:4-dinitrophenylhydrazone	VII
Hydrogenation with Raney Ni & HCl	Addition to benzyl derivative	Addition to benzyl derivative	VII
Acetoacetic ester	Addition	Addition & ring-closure	IV
Cyanoacetic ester	Addition	Addition	III
sym-Tetraphenylacetone	Addition	Addition & ring-closure	IV
Diphenylketene	Addition to δ-lactone	Addition to β-lactone to diene & CO_2 to ring-closure	I
Other ketenes	Addition to α-pyrone	?	II
Vinyl butyl ether	Addition	No addition	VI
PCl_5	Addition to benzoyl derivative	Addition to no benzoyl derivative	V
Benzyl cyanide	Addition	Addition	III

Table XI

proportion of the above types of reactant were tried with 7-benzylideneacenaphthene-8-one (IV) and the results of these trials are summarised in Table XI as far as they are known.

These results show that 7-benzylideneacenaphthene-8-one (IV) undergoes reaction with most of the reagents tried, but in most of these reactions there are variations from the expected. Some of these variations are ring-closures and these can be accounted for by the planar form of the 7-benzylideneacenaphthene-8-one (IV) molecule which forces the reacting atoms into close proximity, but the other variations must be caused by the more fundamental electronic influence of the naphthalene nucleus in the α:β-unsaturated ketone.

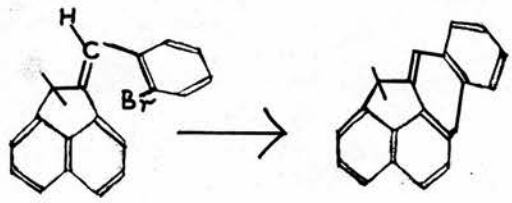
Preparation and Attempted Ring-Closure of 7-(ortho-Bromobenzylidene)-acenaphthene-8-one



III CCXVIII CCX CCXI

7-(ortho-Bromobenzylidene)-acenaphthene-8-one (CCX) was prepared by the condensation of acenaphthene-8-one (III) and ortho-bromobenzaldehyde (CCXVIII) in the presence of a little alkali, and formed yellow crystals melting at 143-5°C.

Attempts were made to ring-close this compound to form 7:8-benz-4:5-ketomethylenephenanthrene (CCXI) by the method used by Reid[253] to ring-close a-(o-halogenobenzylidene)-4:5-methylenephenanthrene,



CCXXI CCXXII

but no product was isolated. J. Stafford obtained a similar result with 7-(ortho-chlorobenzylidene)-acenaphthene-8-one.[280] As it was suspected that the failure of this reaction might be due to the

presence of the carbonyl group in CCX, the compound was reduced by the Wolff-Kishner method[221,222] to form 7-(ortho-bromobenzylidene)-acenaphthene (CCXXI), which formed colourless crystals of M.P. 125-7°C. It was hoped that CCXXI would ring-close to form 7:8-benz-4:5-methylenephenanthrene (CCXXII), but insufficient CCXXI was obtained, owing to partial decomposition during the reduction, and the reactions were consequently discontinued.

EXPERIMENTAL

PART I

SYNTHESES INVOLVING THE CONGENERS

OF 7:8-DIBENZYLIDENEACENAPHTHENE

Introductory Notes

All spectra were observed on a Unicam ultra - violet and visible spectrometer and most are shown in the appropriate sections of the discussion.

Observations of fluorescence were made under a Hanovia ultra - violet lamp.

All melting - points are uncorrected, and were observed on a Kofler micromelting - point apparatus.

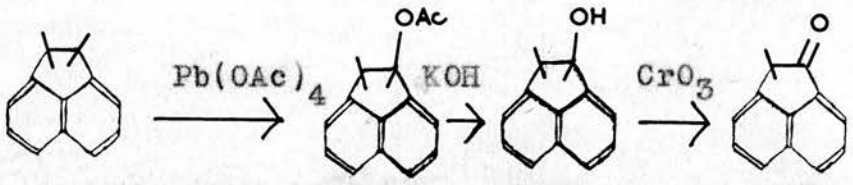
Chromatographic separations were carried out on B. D. H. chromatographic alumina.

Section I

The Use of Diphenylketene

Preparation of Acenaphthene-8-one, III, (p. 7).[39,40]

The method employed was that of Fieser and Cason[39] and consisted of lead tetracetate oxidation of acenaphthene (VIII) to acenaphthenyl-8-acetate (XII), which was hydrolysed to acenaphthene-8-ol (XIII), which in turn was oxidised to acenaphthene -8-one (III), viz.:



VIII XII XIII III

Oxidation of Acenaphthene (VIII) to Acenaphthenyl--8-acetate (XII).[39]

Acenaphthene (77 gm.), M.P. 93-5°C., was dissolved in 550 ml. of glacial acetic acid, which had been freed from aldehydes by distillation over $KMnO_4$, and the solution was placed in a three necked flask fitted with a stirrer and a condenser. 410 Gm. of red lead were then added in 25 gm. portions, with vigorous stirring, over a period of about half an hour, enough time being allowed between the additions of red lead for the red colour to disappear. During the addition, the temperature was carefully maintained between 60°C. &

70°C. When the addition was complete, the mixture was allowed to stand for 10min., by which time a starch-potassium iodide paper was no longer coloured by the solution, showing the oxidation to be complete, and the solution was then poured into one litre of water and extracted with 200 ml. and 150 ml. portions of ether. The combined ether extracts were washed with brine, dried, the ether removed, and the acenaphthenyl-8-acetate (XII) distilled at 137-150°C./0·2 mm.

Hydrolysis of Acenaphthenyl-8-acetate (XII) to Acenaphthene-8-ol (XIII).[39,40]

The distillate from the previous stage was boiled (2 hr.) with a solution of 20 gm. of NaOH in 200 ml. of water and 137 ml. of methanol, and on cooling yielded in two experiments 65.5 gm. (77%) and 66·5 gm. (78%) of acenaphthene-8-ol (XIII) of M.P. 143-5°C. (lit. 144·5-145·5°C.).

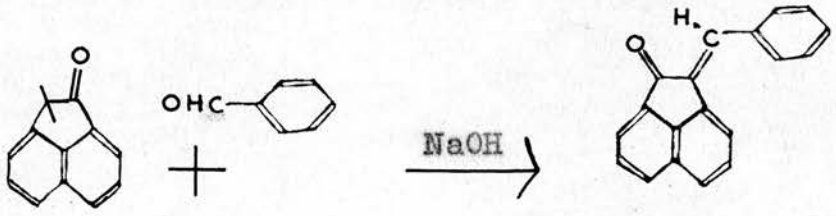
Oxidation of Acenaphthene-8-ol (XIII) to Acenaphthene-8-one (III).[39]

65 Gm. of acenaphthene-8-ol were suspended in 195 ml. of glacial acetic acid and stirred. 28 Gm. of chromic acid anhydride were dissolved in the minimum volume of water and made up to 150 ml. with glacial acetic acid, and this solution was added dropwise to the stirred acenaphthenol suspension over a period of 50 min., while the temperature of the reactants was carefully maintained between 28°C. and 32°C. Stirring was continued for another 40 min., then the solution

was poured into 4 litres of ice-water, stirred, and allowed to stand overnight. The crude acenaphthene-8-one was filtered off, and steam distilled (requires 1-2 weeks) to yield, in two experiments, 40 gm. (61%) and 41 gm. (63%) of acenaphthene-8-one (III) of M.P. 120-2°C. (lit. 121-121·5°C.).

Preparation of 7-Benzylideneacenaphthene-8-one, IV, (p. 9).[51]

The method, based on that of Graebe and Jequier,[51] employs the proportions of reactants found from a large number of experiments to give the best yields. 3·0 Gm. of III were dissolved in 200 ml.



III IV

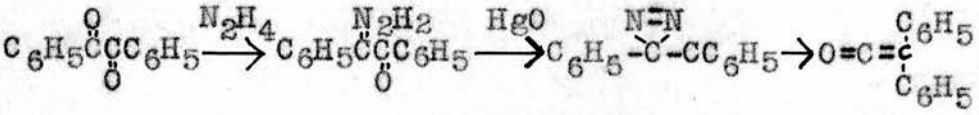
of absolute ethanol and 2 mol. of freshly distilled benzaldehyde were added. Drops of 2N. sodium hydroxide solution were then added until the solution turned red. After several days at room temperature, the crystalline deposit of 7-benzylideneacenaphthene-8-one (IV) was filtered off and dried, giving 3·1 gm. (74%) of product of M.P. 113-115°C. (lit. 117°C.). Recrystallisation from ethanol gave golden leaflets of M.P.116-7°C., whose ultra-violet spectrum was measured (p. 10).

The "almost quantitative" yields mentioned in the literature[51] proved elusive, despite numerous

variations in the method of preparation. It was found that the use of pure dry reagents improved the yield, while the use of a minimum of alkali reduced the quantity of dimeric impurity. This was important as these dimeric products were difficult to remove completely.

Preparation of Diphenylketene, XLII, (p. 29).[130, 131]

The method employed was that of Smith and Hoehn,[130] wherein benzil monohydrazone (CVI) was oxidised, to a diazo derivative CVIII which was then decomposed by heating to form the ketene XLII.



CV CVI CVIII XLII

Preparation of Benzil Monohydrazone (CVI).[129]

22.5 Gm. of an 85% aqueous solution of hydrazine hydrate, when slowly dropped into a hot solution of 79 gm. of benzil (CV) in 150 ml. of ethanol, produced a heavy white precipitate. The suspension was then boiled (5 min.), cooled to 0°C., and the precipitate filtered off, washed and dried to constant weight. The yield was 82 gm. (98%) of benzil monohydrazone (CVI) of M.P. 151°C. (lit. 149-151°C.).

Preparation of Diphenylketene (XLII).[129,127,130,131]

56 Gm. of benzil monohydrazone (CVI)[129] were mixed in a morter with 81 gm. of yellow mercuric

oxide and 35 gm. of calcium sulphate, which had previously been rendered anhydrous by firing for one hour at a red heat. The mixture was then placed in a three necked 1000 ml. flask fitted with a condenser and calcium chloride tube, a mercury sealed stirrer, and a thermometer, and containing 200 ml. of dry, thiophene-free benzene, and was stirred for four hours while the temperature was carefully maintained at 25-35°C. The contents of the flask were filtered, and kept overnight over anhydrous calcium sulphate. The anhydrous diazo-derivative so produced was not isolated, but the benzene solution was filtered through a sintered glass filter into a 250 ml. dropping funnel which was immediately closed with a calcium chloride tube. The dropping funnel was fitted to a 250 ml. Claisens flask, set on an oil bath at 100-110°C. and attached to a vacuum distillation condenser and receiver. The contents of the funnel were allowed to run into the distillation flask over a period of 1½ hours and the benzene was removed with the help of a water-pump, the whole operation being carried out under an atmosphere of nitrogen generated by the decomposition of the diazo-compound (CVIII). The distillation apparatus was then fitted with an air leak, connected to a nitrogen cylinder, and the diphenylketene distilled over at 115-125°C. at low pressure under nitrogen.

Better without water pump - risk of sudden thermal decomposition of diazo cpd which accumulates. - explosive! H.G.H

A yield of 19.6 gm. of diphenylketene (XLII) was obtained and was preserved for use over a period of several months (with the addition of a few crystals of hydroquinone as antioxidant) in a nitrogen filled flask with a well greased ground-glass stopper.

The Interaction of Diphenylketene (XLII) with Chalkone (XVI) on Heating (p. 61).[123,124]

This reaction was carried out, by a method similar to that of Staudinger and Endle,[123,124] as a control experiment for the reaction between 7-benzylideneacenaphthene-8-one (IV) and XLII.

4 Gm. of chalkone and 4 gm. of diphenylketene were placed in a cotton - wool stoppered test - tube, under a stream of nitrogen, and heated at 115-140°C. for 4½ hours in an oil bath. The melt was extracted with ether and allowed to crystallise, yielding 5·3 gm. of crude material of indefinite melting-point. This crude product was a mixture of the δ-lactone of 1:5:4:4-tetraphenyl-1-hydroxy-4-carboxytetramethylene (CXXXIII) and 1:3:4:4-tetraphenylbutadiene (XLIII), and these compounds were crystallised from ethanol, yielding 1·7 gm. of the lactone (CXXXIII), M.P. 191-3°C. (lit. 189-190°C.). The mother liquors were evaporated down and the residues, when crystallised first from petrol, and then from acetone, yielded 1·5 gm. of the butadiene (XLIII), M.P. 145-8°C. (lit. 149-150°C.), which was further purified by boiling with ethanol and potassium hydroxide to remove the remaining lactone. Extraction of the solution

with ether, boiling with charcoal, and crystallisation from ethanol yielded colourless prisms of 1:3:4:4-tetraphenylbutadiene (XLIII), M.P. 152·5-153°C., whose ultra-violet spectrum in ethanol is shown on p. 57.

The Interaction of Diphenylketene (XLII) with 7-Benzylideneacenaphthene-8-one (IV) on Heating (p.29).

2·0 Gm. of each of the reactants were placed in a test-tube through which was passing a stream of nitrogen. The tube was stoppered with cotton-wool and heated in an oil bath for 140 min. at 115-140°C. The warm solution was dissolved in ether, and on standing yielded 0·6 gm. of 7-benzylideneacenaphthene-8-one (IV), identified by M.P. and mixed M.P. Further crystallisation yielded 0·4 gm. of yellow prisms of M.P. 210-250°C. which melted at 243-5°C. after recrystallisation from benzene.

The mother liquors were then evaporated down, the residue dissolved in a minimum of benzene and chromatographed on alumina. Elution with benzene-petrol mixture (1:1) gave rise to:

(a) a red eluate,

(b) and a yellow eluate.

This was followed by elution with pure benzene, which yielded nothing further, and elution with acetone which separated:

(c) a yellow eluate,

(d) and a red eluate.

As all the bands were eluted, the solutions were collected in separate flasks and crystallised.

The red band (a) gave a pale yellow solution with a striking purple fluorescence in ultra - violet light or sunlight, which yielded 0·25 gm. of pale yellow platelets (cpd. A) melting at 273-4°C. after crystallisation from ethanol and benzene.

Experimental analysis: C 94·6% H 5·1%

Theory for $C_{32}H_{20}$ (LXIV): C 95·0% H 5·0%

A mixed melting - point between a specimen of compound A, M.P. 270-1°C., and a specimen of Bergmann's[141] 10:13-diphenyl-11:12-benzfluoranthene M.P. 270-1°C. showed no depression and proved that the compounds were the same.

The eluate of the yellow band (b) gave a deep canary yellow non - fluorescent solution, which on evaporation deposited a mixture of orange prisms of M.P. about 170°C. (compound C) and yellow sugar - like prisms (0·15 gm.) of compound B, M.P. 243-5°C. after crystallisation from acetone, whose analysis suggested an empirical formula of $C_{46}H_{32}O$, corresponding with 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII).

Experimental analysis: C 91·8% H 5·7%

Theory for $C_{46}H_{32}O$ (XLVIII): C 92·0% H 5·4%

The eluate of the yellow band (c) yielded a mixture of unchanged 7-benzylideneacenaphthene-8-one (IV, 20 mg.) and 20 mg. of compound C, M.P. 174-6°C. (decomposed), which was identical with the compound C found in the eluate from (b). Analysis of this compound showed that it had an empirical

formula approximating to that of a dimer of diphenylketene, $C_{28}H_{20}O_2$.

Experimental analysis; C 85·1% H 5·6%

Theory for $C_{28}H_{20}O_2$; C 86·6% H 5·2%

The red eluate (d) on evaporation yielded a few milligrammes of very fine deep orange - red needles, M.P. 296-302°C., which sublimed at 290°C. to deep red needles, but unfortunately there was not sufficient for analysis.

Attempted Hydrogenation of Compound A, 10:13-Diphenyl-11:12-benzfluoranthene, LXIV, (p. 38)[279].

Compound A (10 mg.) in ethyl acetate (10 ml.) was placed in a Tower's microhydrogenator, which had been standardised with stilbene, and subjected to hydrogenation with Adam's PtO_2, and 10% Pt on $BaSO_4$ catalysts. No hydrogen was absorbed with either catalyst and the unchanged LXIV was isolated, and identified by mixed melting - point. Likewise, a qualitative hydrogenation attempted with Raney nickel catalyst failed to change the starting material.

Attempted Decomposition of Compound A, 10:13-Diphenyl-11:12-benzfluoranthene (LXIV) with Ultra - violet Light (p. 26)[103].

To test the stability of LXIV to ultra - violet light, and its resistance to oxidation in the presence of ultra - violet light (cp. Stafford[103]), specimens of the pure compound were exposed to ultra - violet light for ½ an hour in suspension in ethanol, and for two hours in suspension in ether through which oxygen was bubbled. Unchanged

starting material was isolated from both experiments, by evaporation to dryness, and identified by mixed melting - point.

Attempted Hydrogenation of Compound B, 10:10:12:12:13-Pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one, XLVIII, (p. 44).

A specimen of XLVIII in ethyl acetate was subjected to hydrogenation, in a Tower's microhydrogenator, with Adam's PtO_2 catalyst. No hydrogen was absorbed and XLVIII was isolated unchanged at the end of the experiment.

Attempted Preparation of a 2:4-Dinitrophenylhydrazone of 10:10:12:12:13-Pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one, XLVIII, (p. 44).

100 Mg. of XLVIII were boiled under reflux for three hours with excess of 2:4-dinitrophenylhydrazine in ethanol and sulphuric acid (Brady's method). No 2:4-dinitrophenylhydrazone was formed.

Attempted Preparation of a Hydrazone of 10:10:12:12:13-Pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one, XLVIII, (p. 44).

100 Mg. of XLVIII were boiled under reflux with 1 ml. of hydrazine hydrate, 1·5 ml. of toluene and 3 ml. of ethanol for three hours. Only unchanged starting material was obtained, and its identity was shown by mixed melting - point.

Conversion of 10:10:12:12:13-Pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII) into 10:13-Diphenyl-11:12-benzfluoranthene (IXIV) by Heating (p. 47).

Boiling the ketone (XLVIII, 50 mg.) in 5 ml. of

α-methylnaphthalene (B.P. 243°C.) for two hours produced a solution with a brilliant blue fluorescence. Crystallisation yielded 10 mg. of the diphenylbenzfluoranthene (LXIV), MP. 265-270°C., which gave no depression of melting - point when mixed with an authentic sample.

In an attempt to isolate diphenylketene, this experiment was repeated with 0·2 gm. of the ketone (XLVIII), passing a stream of nitrogen through the reaction flask. The nitrogen was passed into aniline, but no evidence of diphenylketene, as its acetanilide[127,157,143], was obtained, though extraction of the α-methylnaphthalene with sodium bicarbonate, followed by acidification of the extract, ether extraction and crystallisation, yielded 2 mg. of diphenylacetic acid, the identity of which was confirmed by mixed melting - point with an authentic sample. 4 Mg. of 10:13-diphenyl-11:12-benzfluoranthene (LXIV) were also isolated by crystallisation of the α-methylnaphthalene residues, and were identified by mixed melting - point.

<u>Identification of Diphenylketene (XLII) as a Product of the Thermal Decomposition of 10:10:12:12:13-Pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one, XLVIII, (p. 50).</u>

To confirm the existence of diphenylketene (XLII) as one of the decomposition products of XLVIII, the microdistillation apparatus shown on p. 181 was used (Fig. 1).

100 Mg. of XLVIII were placed in the bottom of the flask A, wetted with a drop of α-methylnaphthal-

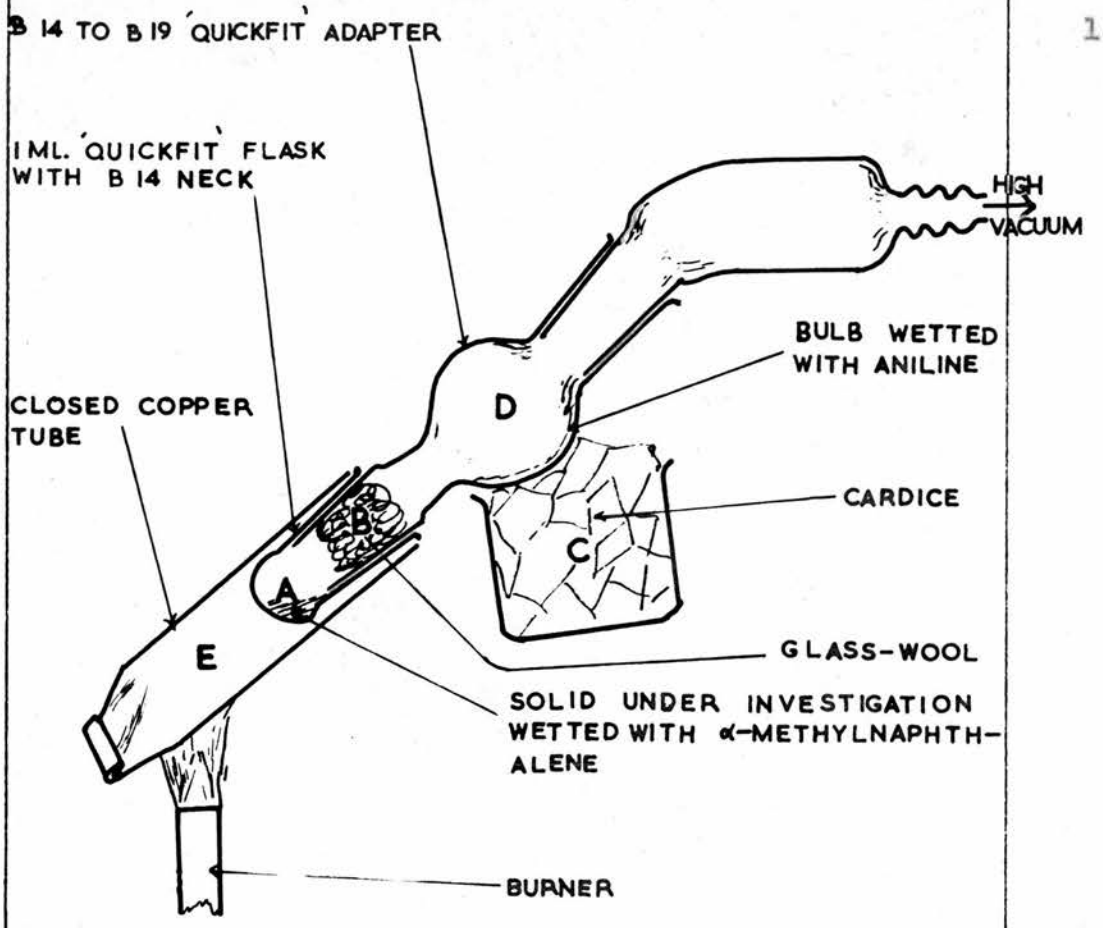


FIG. 1

ene to help to carry over gaseous products, and the adaptor D was inserted, the ground glass surfaces being well lubricated with silicone grease. A little glass - wool was then packed into the neck of the adaptor and flask at B to prevent spurting, all the glass - wool being carefully pushed from the bulb of D into B, and the bulb D was wetted with two drops of freshly distilled aniline, and the apparatus connected to an oil pump. Before commencing the heating, the apparatus was removed from the copper tube, which was heated to about 250°C., while the bulb D was cooled with solid CO_2, after which the apparatus was evacuated. The

flask A was then placed in the neck of the hot copper tube, as shown in Fig. 1. Within a few minutes, the diphenylketene had distilled over, condensing in the bulb D where it immediately interacted with the aniline to form long needles of diphenylacetanilide.[127,157,143] After 20 min., the apparatus was cooled, dismantled, and the cotton - wool and silicone grease removed from B. The diphenylacetanilide and aniline were then washed out, with ether, into a test - tube and crystallised from ether containing a little benzene. 20 Mg. of diphenylacetanilide were obtained, M.P. 179-181°C., and identified by mixed melting - point.

Confirmation of Structure of Compounds A (LXIV) and B (XLVIII) by Condensation of 7-Benzylideneacenaphthene-8-one (IV) and sym-Tetraphenylacetone (LXXVII).

See p. 141 and p. 232.

Decomposition of 10:10:12:12:13-Pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII) with Bases (p. 50).

Attempts to decompose XLVIII with piperidine and aniline in the hope of isolating 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) were ineffectual or indecisive, and the effects of alkali were therefore tried.

100 Mg. of the ketone (XLVIII) were dissolved in 10 ml. of benzene, and 2 ml. of ethanol containing 0·1 gm. of sodium were added. A crimson-red colour with a blue fluorescence was immediately produced (this colour was also produced by the action of strong aqueous - alcoholic potassium hydroxide

solution). The solution was then boiled under reflux for three hours, whereafter it was acidified, made slightly alkaline, and extracted with ether to give a solution with a blue fluorescence. The aqueous portion was then reacidified, extracted with ether, and on evaporation of the ether and recrystallisation of the residue from petrol (B.P. 80-100°C.), yielded 10 mg. of diphenylacetic acid of M.P. 145-9°C., which was identified by mixed melting - point.

The Addition of 7-Benzylideneacenaphthene-8-one (IV) to Diphenylketene (XLII), Using Different Proportions of Reactants (p. 54).

1. 2 Gm. of the ketone (IV) were heated (2½ hours) at 135-145°C. with one mol. (1·6 ml.) of diphenylketene (XLII) in a stream of nitrogen. Crystallisation yielded 0·45 gm. of unchanged ketone (IV), and chromatography of the residues (p.176) yielded 0·25 gm. of 10:13-diphenyl-11:12-benzfluoranthene (LXIV) and a further 0·4 gm. of the ketone (IV). No other product was isolated.

2. 1·0 Gm. of IV was heated at 130-150°C. for 4 hours under nitrogen with 4 mol. (3·2 ml.) of diphenylketene. Crystallisation yielded 1·5 gm. of 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII), and chromatography (p. 176) yielded 0·5 gm. of 10:13-diphenyl-11:12-benzfluoranthene (LXIV). No other product was isolated.

In both the above experiments, the identities of the products were confirmed by mixed melting -

points, and the results of the experiments are summarised in Table III.

No. of Expt.	Ratio of mol. of XLII:IV	Time of Expt.	Wt. of Products (gm.)			Percentages of Products		
			IV (Ketone)	XLVIII (Phl)	LXIV (Diphl-F)	IV	XLVIII	LXIV
1	1:1	2½hr.	·85	0·0	0·25	43	0	8
2	1:4	4hr.	0.0	1·5	0·05	0	64	3

Table III

The Isolation of 7-Benzylidene-8-diphenylmethylene-acenaphthene, XXXII, (p. 58).

The decomposition of 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (XLVIII) by the action of alkali has been described on p.182.

The neutralised red residues from this decomposition were dissolved in benzene, adsorbed on alumina and eluted with petrol. No crystals were obtained from the red eluate, and as it was thought that it might contain some ethanol, which might carry impurities through the column, the eluate was evaporated down under high vacuum, dissolved in the minimum of petrol, and again adsorbed on alumina, giving a red band. The column was developed with petrol (B.P. 40-60°C.), which caused very slow movement of the red band, and was eluted with this solvent to remove impurities. The red band was then eluted with petrol (B.P. 60-80°C.). This produced a crimson-red solution with a blue fluorescence, which on evaporation yielded an oil that

could not be crystallised from petrol or ethanol, even at the temperature of solid carbon dioxide - acetone mixture.

The qualitative ultra - violet and visible spectrum of the solution of 7-benzylidene-8-diphenylmethyleneacenaphthene (XXXII) was then observed, using spectroscopically pure cyclohexane as solvent, and is compared on p. 56 with the spectrum of a less rigorously purified specimen of XXXII dissolved in chloroform. The spectra are similar, though the less pure specimen shows signs of the peaks at 407 mμ. and 384 mμ. associated with the spectrum of 10:13-diphenyl-11:12-benzfluoranthene, LXIV, (p. 41).

As the spectra of XXXII are qualitative, no reliable ϵ values can be shown, but assuming that the peak at 365 mμ. has an ϵ value typical of that for a naphthalenic compound,[121] estimated ϵ values can be arrived at for XXXII, and are shown on p. 56.

Attempted Clemmensen Reduction of 10:10:12:12:13-Pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one, XLVIII, (p. 67).[158,159,160]

Amalgamated zinc (2 gm.), water (1 ml.) and conc. HCl (3 ml.) were boiled (90 hr.) in a 25 ml. flask with 0·4 gm. of XLVIII, dissolved in 2 ml. of toluene, with the addition during the reaction of three further 1 ml. portions of conc. HCl. The aqueous and toluene layers were separated, and the former extracted with ether, the extract being

added to the toluene layer, which was then dried and the solvent removed. Crystallisation from benzene-petrol mixture yielded 10 mg. of colourless crystals of M.P. 235-9°C., which sublimed at about 200°C., and on recrystallisation melted at 245-6°C.

Experimental Analysis: C 86·2% H 5·3% M.W. 278

Theory for $C_{28}H_{20}O_2$: C 86·6% H 5·2% M.W. 388.4

Apart from the molecular weight, the analysis supports the supposition that the compound is 2:2:4:4-tetraphenylcyclobutane-1:3-dione (XLIX).

The combined mother liquors from the above crystallisations were evaporated down to yield an oil, which was then dissolved in petrol, and chromatographed on alumina. Elution with petrol and benzene produced several coloured bands, followed by a yellow band containing about 0·1 gm. of a yellow oil. By careful crystallisation of this oil from ethanol containing a little ether, further small quantities of the compound of M.P. 245-6°C. were isolated, along with elongated canary yellow prisms of M.P. 186-191°C. Recrystallisation of this compound raised the melting-point to 192-4°C., and it was analysed, and its ultra-violet spectrum observed (p. 69).

Experimental analysis: C 89·4% H 5·6%

<u>The Effect of γ-Radiation on 10:10:12:12:13-Pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one, XLVIII, (p. 68).</u> [147]

Two glass stoppered 30 ml. weighing bottles were filled with a solution made from 10 mg. of pure ketone (XLVIII) in 'AnalaR' benzene (70 ml.),

and both solutions were examined under ultra - violet light and found to have the same dull purplish appearance. One solution was then preserved in a dark place as a control, and the other was placed within one inch of the centre of the approximately 100 curie Co^{60} radiant source which was available at the Edinburgh University Chemistry Department.

The radiation of the Co^{60} source had the effect of darkening the glass of the weighing - bottle after four hours, however the solution appeared unchanged in ultra - violet light, but after 24 hours the solution showed a slight but definite blue fluorescence in ultra - violet light which was not shown by the control. After a total of 48 hours exposure to the Co^{60} source, the blue fluorescence of the solution was observed to have increased, but was insufficient to suggest that there was any chance of isolating any 10:13-diphenyl-11:12-benzfluoranthene (LXIV) which might have been formed. The solution was therefore exposed for a further fortnight to the radiant source, after which it was removed and examined.

The solution was now a yellowish - brown colour, with a slight brownish deposit, and had a deep blue fluorescence in ultra - violet light. Chromatography of this solution using petrol and petrol containing 33% benzene as eluents yielded a few milligrammes of crystals, M.P. 234-6°C., of unchanged starting material (confirmed by mixed melting - point), and a very small quantity of very thin colourless plates of M.P. 55°C. Recrystallisation of

this substance gave a melting - point of 58-60°C., and it was thought that the compound might be diphenyl (M.P. 71°C.) which is believed to be produced by the exposure of benzene to radioactivity.[147, 273, 269] No trace of 10:13-diphenyl-11:12-benzfluoranthene (LXIV) could be found.

Attempted Cyclodehydrogenations of 10:13-Diphenyl-11:12-benzfluoranthene[136], LXIV, (p. 70).

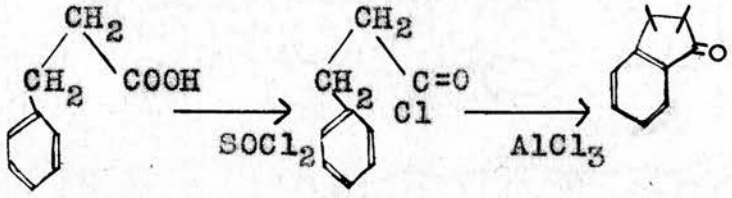
1. 50 Mg. of LXIV were dissolved in 5 ml. of α-methylnaphthalene, and boiled under reflux with 3 mg. of Adam's PtO_2 catalyst for 24 hours. At the end of this time, the blue fluorescence of the solution was slightly darker, but on evaporation of the α-methylnaphthalene, the only product that was isolated was unchanged LXIV of M.P. 272-3°C., the identity of which was confirmed by mixed melting - point.

2. 50 Mg. of LXIV were dissolved in 5 ml. of α-methylnaphthalene, and boiled under reflux with 15 mg. of 30% palladium on charcoal catalyst. After refluxing for 24 hours, the reactants were placed on a metal bath, and after heating up to 320°C., the residue was worked up. The only product that could be isolated was unchanged LXIV of M.P. 268-271°C., the identity of which was confirmed by mixed melting - point.

The Action of Diphenylketene on 2-Benzylidenehydrindene-3-one

Preparation of Hydrindene-3-one, XCIX, (p. 74).[151,152,153]

This compound was prepared by the ring - closure of β-phenylpropionyl chloride (XCVIII) with anhydrous $AlCl_3$.



XCVII XCVIII XCIX

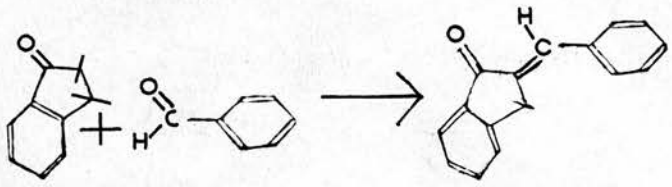
The β-phenylpropionyl chloride (XCVIII) was prepared by gently heating 50 gm. of β-phenylpropionic acid (XCVII) with an equal weight of thionyl chloride for two hours in a flask fitted with a reflux condenser. After two hours, the excess of thionyl chloride was removed by heating in a water bath, under 25 mm. pressure, and the product was distilled to yield 53 gm. (95%) of the acid chloride, B.P. 121-2°C.

The ring - closure was effected by dissolving 50 gm. of the acid chloride (XCVIII) in 200 ml. of petrol (B.P. 60-80°C.), and adding 50 gm. of finely powdered anhydrous $AlCl_3$ to the solution. The reaction was carried out in a 3 litre flask to avoid loss from the vigorous initial evolution of HCl gas. Once the vigorous initial evolution of

HCl had subsided, the volume of solvent was made up to 200 ml., and the flask heated in a water-bath until the lower layer became very thick and brown (20-30 min.), when the contents of the flask were cooled, and the $AlCl_3$ complex decomposed with ice. The crude hydrindene-3-one (XCIX) was crystallised, extracted with ether, the extract filtered and dried, and the ether removed to give 20 gm. of product (51% yield).

Preparation of 2-Benzylidenehydrindene-3-one, LXXX, (p. 74).[149,150]

This was prepared by dissolving the hydrindene-3-one (XCIX) in ethanol, adding excess benzaldehyde (1·3 mol.), and adding alcoholic KOH dropwise till the colour of the resulting solution darkened. Crystals of the crude benzylidene compound (LXXX) separated out overnight, and on crystallisation gave a poor yield (10%) of pure product, M.P. 110·5-111°C. (lit. 109-110°C.).



XCIX LXXX

The Reaction of Diphenylketene (XLII) on Heating with an Equimolecular Proportion of 2-Benzylidene-hydrindene-3-one, LXXX, (p. 74).[130,131]

Two experiments were carried out in which 1·0 gm. and 0·8 gm. of the benzylidene-compound (LXXX) were heated in cotton-wool stoppered test-tubes in an oil-bath at 135-145°C. and 140-150°C., respectively,

for 2½ hours under a stream of nitrogen, with 1·0 and 1·3 mol. of XLII, respectively. The hot syrup was dissolved in ether and was then crystallised from ethanol to give 40% and 50% yields, respectively, of colourless crystals. These crystals gave a bright yellow solution in ethanol and melted at 136·5-139°C. yielding a bright yellow melt, but they did not fluoresce in ultra - violet light. The compound was purified for analysis and spectroscopy by crystallisation from ethanol and finally petrol, the ultra - violet spectrum being observed in ethanolic solution and as a film formed by evaporating the solution on the walls of the silica cell that was used for the spectroscopic measurements (p. 80).

From the first reaction, about 20 mg. of pale yellow prisms, melting at 230-231·5°C. and subliming from about 222°C., were obtained by trituration of the mother liquors with chloroform - petrol and chloroform - ether mixtures.

The analysis of the compound of M.P. 136·5-139°C. was:-

Experimental analysis; C 93·2% H 5·8%

Theory for $C_{29}H_{22}$ (LXXXIII); C 94·0% H 6·0%

which accords reasonably with the composition of 3-diphenylmethylene-2-benzylidenehydrindene (LXXXIII).

The analysis of the compound of M.P. 230-231·5°C. was:-

Experimental analysis; C 88·4% H 5·9%

Theory for $C_{43}H_{32}O$ (LXXXIV): C 91.5% H 5·7%

and is compared with that of compound LXXXIV (p.86).

Hydrogenation of 3-Diphenylmethylene-2-benzylidene-hydrindene, LXXXIII, (p. 79).

8·13 Mg. of LXXXIII in 10 ml. of ethylacetate were hydrogenated in a Tower's microhydrogenator at room temperature. The yellow solution was hydrogenated till it became virtually colourless (1½ hours), when the shaker was stopped and the uptake of hydrogen measured. The shaker was then restarted, but no further significant uptake of hydrogen occurred. The volume of hydrogen absorbed, corrected to N.T.P., was 0·477 ml., and represented an uptake of 0·97 mol.

The colourless solution produced had a blue fluorescence and yielded a colourless oil from which no pure product was isolated, even when the reaction was repeated with larger quantities.

Oxidation of 3-Diphenylmethylene-2-benzylidenehydrindene (LXXXIII) with Chromic Anhydride in Glacial Acetic Acid (p. 82).

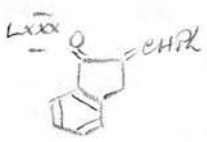
1·0 Gm. of chromic anhydride, dissolved in the minimum of water, was added to 50 ml. of "AnalaR" glacial acetic acid. The solution was slowly run into a solution of 0·1 gm. of LXXXIII, dissolved in the minimum volume of "AnalaR" glacial acetic acid, and the rapid disappearance of the colour of the chromic anhydride showed that a reaction was occurring. When an excess of the chromic anhydride solution, as indicated by its colour, had been run in, the reaction mixture was allowed to

stand for ½ an hour in the cold. The solution was then heated on a water bath and chromic anhydride solution run in till there was a permanent yellow colour, and the reactants were kept on the water bath for two hours longer. After this, 50 ml. of water were added, and the solution was extracted with ether. The ether extract was partially neutralised with KOH and was then extracted with $NaHCO_3$ which was in turn acidified and extracted with ether to give an acidic fraction which did not yield any crystalline product. The original ether extract containing the non-acidic fraction, however, yielded an oil smelling of benzophenone (CXXX), which would not crystallise, but which on treatment with 2:4-dinitrophenylhydrazine yielded 10 mg. of the 2:4-dinitrophenylhydrazone of benzophenone, red needles of M.P. 240-2°C., which was identified by mixed melting-point with an authentic specimen.

The Addition of 2-Benzylidenehydrindene-3-one (LXXX) to an Excess of Diphenylketene, XLII, (p. 75).

1·0 Gm. of the ketone (LXXX) was heated under a stream of nitrogen at 150-160°C. for four hours with 5 ml. of diphenylketene. When the reaction was complete, ether was added to the hot solution which on crystallisation yielded 1·9 gm. of colourless crystals of indefinite melting-point

(about 170°C.). On further crystallisation from chloroform-ether mixture, these crystals deposited colourless needles, melting at 245-6°C. to a colourless melt which decomposed at about 300°C. Crystallisation of the mother liquors gave no further product, and they were therefore chromatographed on alumina. On crystallisation of the eluate obtained with benzene-petrol mixture, colourless crystals were deposited which melted, with evolution of gas, at 228-9°C. giving a yellow oil.



A mixed melting-point between the compound of M.P. 245-6°C. and the dimer of LXXX (lit. M.P. 244°C.) showed a depression to 212°C., proving these two compounds were not identical. Analysis of the compound of M.P. 245-6°C. agreed with the suggested 2:2:4:4-tetraphenylcyclobutane-1:3-dione (XLIX) structure, and a mixed melting-point between a specimen of this compound and the compound of M.P. 245-6°C. isolated from the attempted Clemmensen reduction of XLVIII (see p.68). proved the identity of these two compounds.

Experimental Analysis: C 86.4% H 5.3%

Theory for $C_{28}H_{20}O_2$ (XLIX): C 86.7% H 5.2%

An attempt to produce a 2:4-dinitrophenylhydrazone from the compound M.P. 245-6°C. was unsuccessful.

Analysis of the compound of M.P. 228-9°C. accorded only moderately with the suggested structure of 1:2:2:4:4-pentaphenyl-1:2:3:4- tetrahydrofluorene-3-one (LXXXIV).

Experimental Analysis: C 89.4 H 5.9%

Theory for $C_{43}H_{32}O$ (LXXXIV): C 91.5% H 5.7%

Identification of Diphenylketene (XLII) as a Product of Decomposition by Heating of the Compound of M.P. 228-9°C. (1:2:2:4:4-Pentaphenyl-1:2:3:4-tetrahydrofluorene-3-one, LXXXIV), see p. 86 .

This reaction was carried out in the same manner as that used with compound XLVIII (p. 180)

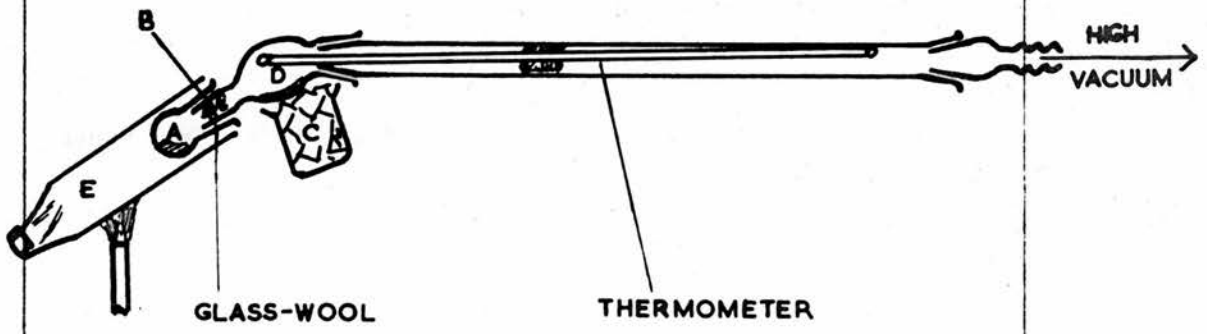


FIG. 2

(FOR LEGEND SEE FIG. I P. 181.)

using the apparatus shown in Fig. 2. 20 Mg. of LXXXIV were heated at about 250°C. in high vacuum and yielded 5 mg. of diphenylacetanilide[127,157,143] of M.P. 182°C., the identity of which was established by mixed melting-point with a known specimen.

The residue in the bulb was crystallised from benzene-petrol mixture and yielded a few milligrammes of colourless crystals of M.P. 230°C. which were proved by mixed melting-point to be unchanged LXXXIV. A yellow oil was left which would not crystallise.

The Effect of Heating the Compound of M.P. 245-6°C. (2:2:4:4-Tetraphenylcyclobutane-1:3-dione, XLIX), see p. 82.

This reaction was carried out in exactly the same manner as that used above with the compound of M.P. 228-9°C. 20 Mg. of XLIX were heated in high vacuum at about 250°C. with a little aniline in the cooled collecting bulb. A liquid distilled over into the collecting bulb, and on crystallisation deposited colourless crystals of M.P. 244-7°C., which were proved by mixed melting-point to be unchanged starting material. No other product could be isolated. A study of the compound melting at 245-6°C., under the microscope of a hot stage micromelting-point apparatus, showed that the compound decomposed with evolution of gas at about 300°C.

Hydrolysis of the Compound of M.P. 245-6°C. (2:2:4:4-Tetraphenylcyclobutane-1:3-dione, XLIX), see p. 84.

125

50 Mg. of XLIX were heated overnight on a water bath with 2 ml. of 2N NaOH solution, 5 ml. of benzene and 5 ml. of ethanol. An ether extraction was carried out with the residue and yielded, on crystallisation, copius quantities of very fine colourless needles which, on crystallisation from petrol, gave a melting-point of 133·5-135°C. (lit. M.P. for sym-tetraphenylacetone is 135°C.).

The analysis of the compound of M.P. 133·5-135°C. confirmed its identity as sym-tetraphenylacetone

(LXXVII), apart from the molecular weight which, however, differed from the molecular weight determined from the percentage of residue. 197

Experimental analysis: C 89.8% H 6.4% MW. 256

Theory for $C_{27}H_{22}O$ (LXXVII): C 89.5% H 6.1% MW. 362

Section 2

The Use of Ketene and Phenylketene

Preparation of Phenylketene, CX, (p. 96)[169].

Mandelic acid (CXIV), with phosphorus pentachloride, yields phenylchloracetyl chloride (CXV), which with metallic zinc loses chlorine to form phenylketene (CX).

75 Gm. of mandelic acid were heated at 120-140°C. for 3½ hours with 208 gm. of PCl_5. After standing overnight, the contents of the flask were distilled in high vacuum to give the crude acid chloride (CXV) which was purified by re-distillation, giving 38 gm. (41%) of CXV, B.P. 136-142°C./80 mm.

$$\underset{\text{CXIV}}{PhCHOHCOOH} \xrightarrow{PCl_5} \underset{\text{CXV}}{PhCHClCOCl} \xrightarrow{Zn} \underset{\text{CX}}{PhCH=C=O}$$

The acid chloride (25 gm.) in dry ether (200ml.) was quickly added to 20 gm. of dry zinc in a separating funnel from which air was excluded by a flow of nitrogen. On gentle warming, a vigorous reaction started, giving a yellow solution which became turbid after about 15 min. The solution was kept for a further 5 min., then boiled for 20 min., 50ml. more ether being added. Dry petrol (B.P. 40-60°C.),

400 ml., was then added to precipitate the zinc chloride formed. The brown oily layer containing the zinc chloride was run off, and the pale yellow solution containing the phenylketene (CX) was run straight in to the reaction flask containing the previously prepared reaction mixture, and used immediately.

The Interaction on Heating 7-Benzylideneacenaphth-[39,51] ene-8-one (IV) with Phenylketene, CX, [169] (p. 96).

150 Ml. of the phenylketene (CX) solution prepared above were added to the ketone IV (1 gm.) in dry benzene (5 ml.). After the removal of solvent, the mixture was heated to 120-140°C. for four hours, and yielded a red-black tar which did not crystallise from ether-benzene mixture. The product was therefore dissolved in the minimum of benzene and chromatographed in the benzene on alumina. A proportion of the tar did not dissolve in benzene, and was dissolved separately in acetone in which it gave an intensely red solution, but from which it did not crystallise. Chromatography of the fraction insoluble in benzene, with dioxan as eluent, followed by crystallisation, gave the same result. A black band remained on this column and could not be removed with either acetone or dioxan.

The chromatography of the benzene soluble part of the tar gave, on elution, the following fractions:

1. With petrol (B.P. 80-100°C.), a brown solution with a striking blue fluorescence was

produced, from which a small quantity of an oil was obtained, but no crystalline product.

2. With 50% petrol (B.P. 40-60°C.) in benzene, a yellow band was removed which, on crystallisation from alcohol and acetone, gave a few milligrammes of unrecognised yellow crystals of M.P. about 80°C.

3. With benzene, a yellow-brown solution was produced, which did not crystallise.

4. The column still contained a black band, which was extruded, and extracted with ether in a Soxhlet extractor to give a deep red coloured solution.

5. Soxhlet extraction of that part of the black band which was not removed with ether was repeated, using acetone, and yielded a black uncrystallis able oil.

Attempts to crystallise the above fractions were unsuccessful, except in the case of '2', where there was insufficient solid to purify. The red coloured fraction (4) from the chromatogram was the largest, and after attempts to crystallise this from acetone had failed, it was re-chromatographed, and a blue-black and a brown band were eluted with dioxan, but no crystals were obtained. The residues were then dissolved in phosphoric acid and petrol, and on dilution of the cherry red acid layer with water, a blue solution with a slight precipitate was formed, but again no crystals were obtained.

The colour of this red substance varied with the solvent in which it was dissolved, ranging from cherry red in syrupy phosphoric acid solution, in which it was quite soluble, through deep red in very slightly acidic solution, and blue-green to almost black in solution in ethanol, or toluene which had been standing over sodium, finally to yellow in a solution containing NaOH.

The Interaction on Heating Chalkone (XVI) with Phenylketene (CX)[169], p. 96.

Chalkone (1·0 gm.), dry benzene (5 ml.) and 150 ml. of the phenylketene (CX) solution prepared above (p. 198) were mixed. After the removal of solvent, the mixture was heated at 120-140°C. for four hours, and yielded a red-black tar which did not crystallise from ether-benzene mixture. The benzene soluble part of the tar was then chromatographed on alumina and developed with petrol-benzene (1:1), and the following fractions were eluted:

1. With 50% petrol in benzene, a yellow band was eluted, which on crystallisation from petrol-benzene mixture gave only a very few yellow crystals, which could not be studied further.

2. With benzene, a yellow oil was obtained which gave no solid.

3. With ether, a yellow oil was first obtained from which nothing could be crystallised, but this was followed by a maroon solution which gave dark red crystals, M.P. 234-240°C. Re-crystallisation of this product from acetone yielded about

20 mg. of red-black needles which had a golden lustre, and melted at 236-238°C. These were analysed.

4. With acetone, a dark solution which gave a brownish solid was eluted, but no other product was isolated.

The part of the original product that was insoluble in benzene was dissolved in acetone and purified by boiling with charcoal, but no pure product was obtained on crystallisation.

The colour of the red compound was found to depend on the pH of the solution, and on the type of solvent. The crystals gave a red-violet solution in chloroform (violet in aqueous-acetone), which on the addition of a drop of acid became red (yellowish in aqueous-acetone), this colour change being reversed on the addition of ammonia.

Analysis of the compound of M.P. 236-8°C. gave:-

Experimental analysis: C 87·0% H 4·7%

Theory for $C_{23}H_{18}O_2$: C 84·6% H 5·6%

(1 Mol. XVI plus 1 mol. phenylketene).

The solution was too dark for a molecular weight determination.

The Preparation of Ketene, CIX, (p. 96).[170,171,174]

Ketene (CIX) was prepared by passing acetone vapour over a red-hot wire. The apparatus used was simpler to make and more convenient than some of those described in the literature,[174] and is therefore shown in Fig. 3. The heating element consisted of a spiral of four metres of 24 guage nickel-chromium wire held by eight glass hooks attached to the centre tube of the apparatus, and held apart by

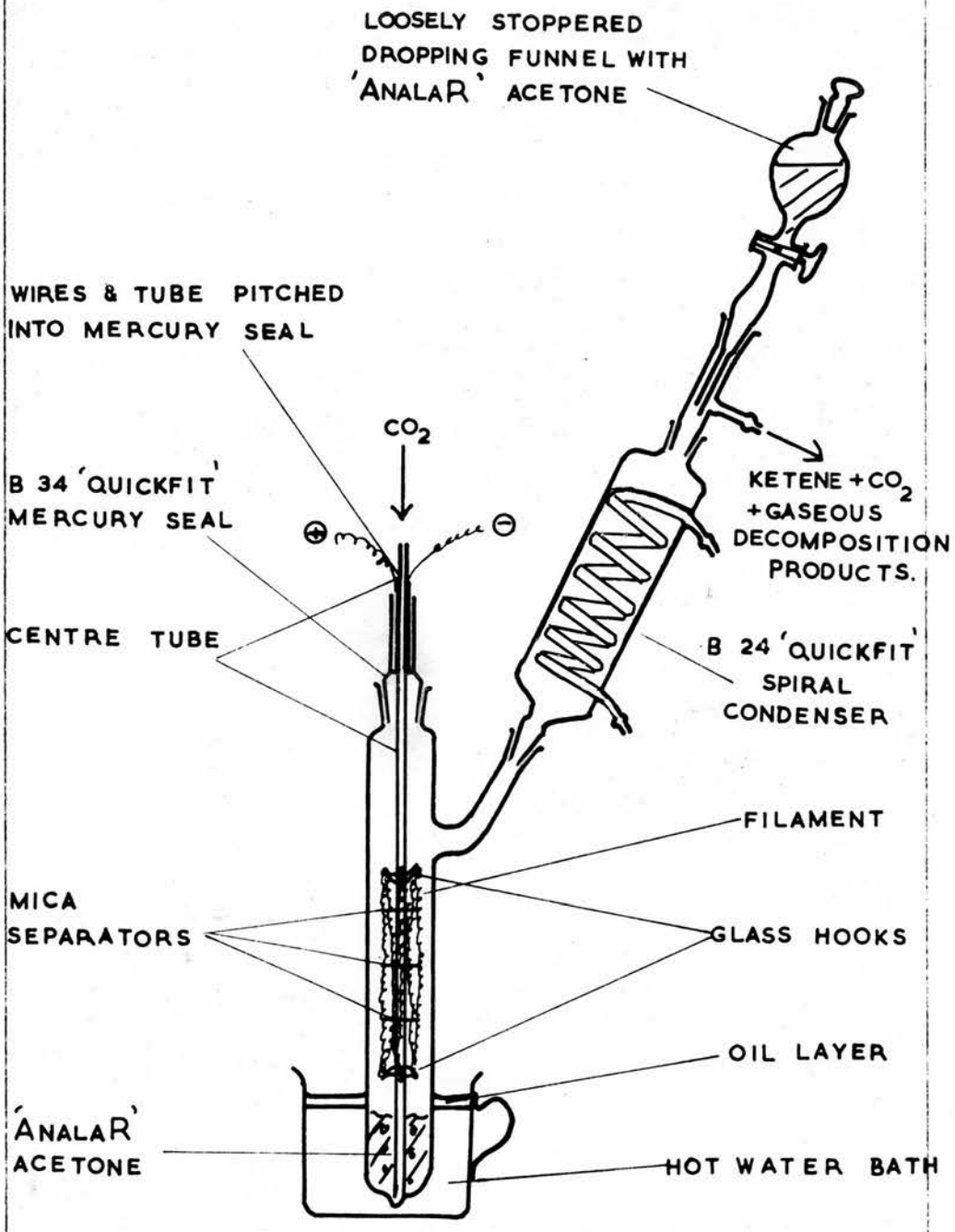


FIG. 3

KETENE GENERATOR

mica separators. The rest can be seen from the figure.

To use the apparatus, it was first flushed with CO_2, then the filament was heated electrically

to a full red heat (at lower temperatures, excessive carbon was deposited on the filament, which was consequently short circuited), then the "AnalaR" acetone was heated on a water bath (covered with oil to reduce the emission of water vapour) and ketene was generated. To test the apparatus, the ketene produced was led into an ethereal solution of aniline, and it was found, by isolating and weighing the acetanilide formed, that 30 gm. of ketene were produced per hour.

<u>The Effect of Treating Chalkone (XVI) with Ketene,</u> [170, 174, 171 CIX, (p. 96).]

1. 1 Gm. samples of chalkone in 12 ml. of acetone were treated for 5 minute periods by passing ketene, at a rate of 30 gm. per hour, through the solutions. Three experiments were carried out this way, at temperatures of 28°C., 80-100°C., and 217-9°C., but only unchanged starting material (XVI) was obtained at the end of each experiment, and identified by mixed melting-point. Excess ketene was destroyed by drawing it into a water-pump.

2. Ketene was passed into 5 gm. of molten chalkone at 180-200°C. at a rate of 30 gm. per hour for two hours. Excess ketene was destroyed by drawing it into a water-pump. At the end of the reaction, the melt was brownish and part of its mass had been lost, presumably by distillation of XVI into the gas stream at the high temperature used. The residue did not crystallise, and was therefore

chromatographed on alumina, but unchanged starting material, identified by mixed melting-point, was the only product to be isolated.

The Effect of Treating Chalkone (XVI) with Ketene (CIX) in the Presence of a BF_3 Catalyst (p. 99).

See Part II, Section 6, (p.246).

The Effect of Treating Chalkone (XVI) with Ketene[170,171,174] (CIX) in the Presence of Zinc Chloride (p. 99).

Chalkone (1·0 gm. in a little acetone) with $ZnCl_2$ (0·2 gm.) was treated with ketene (CIX) at a rate of 30 gm. per hour for 19 min. Ketene was passed in the cold for the first 3 min., then the mixture was heated to 200°C. over the next 8 min., then to 230°C. over the following 8 min., whereafter acetone was added and the mixture cooled. At about 140°C., the melt started to darken and at the end of the reaction was dissolved in phosphoric acid containing a little ether, and gave a brown fluorescent solution when extracted with petrol. No pure product was obtained.

The Effect of Treating 7-Benzylideneacenaphthene-8-one[51] (IV) with Diphenylketene[127,130,131] (XLII) in the Presence of Zinc Chloride (p. 99).

2 Gm. of the ketone (IV, in 30 ml. of dry ether) with 1·6 ml. of diphenylketene and 0·5 gm. of $ZnCl_2$ were kept for one hour under a slow flow of nitrogen. There was no apparent change, and the mixture was gradually heated to 150°C., at

which it was maintained for 1½ hours. The product was extracted with ether and crystallised from ether and ethanol to yield 0·7 gm. of unchanged IV, identified by mixed melting-point. Further crystallisation from petrol gave 1·7 gm. of diphenylacetic acid, identified by mixed-melting point. When the residues from the crystallisations were chromatographed on alumina, after extraction with $NaHCO_3$ to remove diphenylacetic acid, a few milligrammes of a fluorescent oil were isolated, which presumably contained 10:13-diphenyl-11:12-benzfluoranthene (LXIV). No red coloured compound was present.

Condensation with Benzyl Cyanide

Condensation of 7-Benzylideneacenaphthene-8-one (IV)[51] with Benzyl Cyanide, CXLV, (p. 102).[192,186,255]

Benzyl cyanide (0·23 ml., 1 mol.) was added to the ketone (0·5 gm.) in dry ether (4 ml.) and dry ethanol (6 ml.) containing 0·077 gm. of potassium. The solution, which became deep red, was boiled under reflux for two hours, then acidified with HCl to give a yellow precipitate which on crystallisation from ethanol yielded colourless crystals of M.P. 190-215°C.

The crystals were separated by repeated crystallisations from chloroform-petrol mixture into colourless prisms of M.P. 204-8°C. and colourless needles of M.P. 218-221°C. Both of these were shown by the Lassaigne test to contain nitrogen, and by analysis to be isomeric 7-benzylidene-8-(w-cyanobenzyl)-acenaphthene-8-ols (CXLVI).

Prismatic crystals, M.P. 204-8°C.:-

Experimental Analysis: C 86·9% H 5·1%

(Nitrogen was present, but was not determined.)

Theory for $C_{27}H_{19}ON$

(CXLVI): C 86·8% H 5·1% N 3·8% O 4·3%

Needle shaped crystals M.P. 218-221°C. (melting-points up to 230°C. were also observed):-

Experimental Analysis: C 86·6% H 5·3%

(Nitrogen was present, but was not determined.)

Theory for $C_{27}H_{19}ON$

(CXLVI): C 86·8% H 5·1% N 3·8% O 4·3%

Only a small combined yield (about 3%) of the separated products was obtained, and later attempts to separate the crude product by hand, and by heating the mixture of crystals on filter paper till the lower melting-point product melted and was absorbed, and thus could be separated, were of limited success, while attempts at separation by chromatography on alumina, using benzene-petrol mixture as eluent, were unsuccessful. It was necessary in later experiments, therefore, to use the unseparated product mixture purified by crystallisation from acetone.

Variations of the above method of preparation were tried, and are summarised in Table V below.

Wt.of IV gm.	Solvent	Catalyst	Time hr.	Temp.	Yield
0·5	-	Piperidine	3½	cold	-
		2 ml.	2½	reflux	60% "Q"
0·5	10ml.EtOH	K, 0·5 gm.	46	cold	-
			100	cold	-
0·5	10ml.EtOH	K, 0·5 gm.	16	cold	36% "P"

Table V (Continued overleaf).

Wt.of IV gm.	Solvent	Catalyst	Time hr.	Temp.	Yield
0•5	Benzene & EtOH	K, 0•5 gm.	5	cold	42•5% "P"
0•5	10ml. EtOH 2ml. Et_2O	K, 0•5 gm.	8½	cold	43•5% "P"
3•0	60ml. EtOH	K, 3•0 gm.	7	warm	59% "P"

Legend: "P" - Mixed Product CXLVI

"Q" - Unchanged IV.

Table V

Attempted Dehydrations of the Product Mixture from the Condensation of 7-Benzylideneacenaphthene-8-one (IV) with Benzyl Cyanide, CXLV, (p. 103).

A large number of reactions were carried out, and are summarised in Table VI below. The various products obtained are described by the legend opposite the Table.

See Overleaf.

Legend:-

IV, 7-Benzylideneacenaphthene-8-one, produced by decomposition.

"H", Apparently unchanged mixture of starting materials.

"J", Colourless compound of M.P. 273°C.

Analysis; C 71·5% H 2·9%

"K1" Colourless compound of M.P. 218-228°C. (Mixed melting-points with "J" and with starting material showed depressions.)

Analysis;

C 85·6% H 5·1% N 3·1% Cl 0·0%

"K2" Colourless compound of M.P.218-220°C. (Mixed melting-points with "K1" and starting material were indefinite, though analysis would suggest this was same as "K1").

Analysis;

C 86·1% H 5·1% N 3.3% M.W. 256

"L" Colourless compound of M.P. 247-252°C. Sublimes about 240°C.

"M" Reddish needles of M.P. 213-214°C., subliming about 190°C. There were traces of a red colouration from several of the reactions, notable especially during chromatography.

Table VI

The difficulty of obtaining pure products with sharp melting-points made certain identification of

the products impossible, and this work was therefore discontinued.

[139,156]

Preparation of 2:4-Dinitrophenylhydrazone of Compound "K2" (p.104).

The compound "K2" M.P. 218-220°C., (see above) formed a 2:4-dinitrophenylhydrazone by Brady's [156] method (after 3 hr. boiling) which crystallised from tetralin to form red plates of M.P. 259-261°C.

Experimental Analysis; N 16·1%.

EXPERIMENTAL

PART II

THE REACTIONS OF

7-BENZYLIDENEACENAPHTHENE-8-ONE

AND THE PREPARATION OF 10-PHENYL-

FLUORANTHENE DERIVATIVES

Section IV

Condensation Reactions

Preparation of 7-Benzylideneacenaphthene-8-one IV[51] (p. 9).

See p. 172.

Condensations of 7-Benzylideneacenaphthene-8-one with Acetoacetic Ester

Preparation of 10-Phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one (LXV) and 10-Phenyl-11-carbethoxy-9:10:11:12-tetrahydrofluoranthene-12-one[57], CLVI, (p. 109).

The general method of the synthesis was to keep a solution of 7-benzylideneacenaphthene-8-one (IV) in absolute ethanol standing at room temperature, or boiling under reflux, with acetoacetic ester (CLI) in the presence of one mole of sodium (as its ethoxide) or a quantity of piperidine or other amine, which acted as a catalyst.[57,224] A number of reactions were carried out and the details of the experimental conditions and results are summarised in Table X.

The crude reaction product, obtained as a yellow precipitate by acidifying the reaction

mixture with HCl, was filtered off and crystallised from either ethanol or benzene-petrol mixture. The principal product from each reaction formed canary yellow prisms of M.P. 180-181·5°C. (LXV), while varying small quantities of the compound melting at 160-2°C. (CLVI) were obtained as pale yellow needles by further crystallisation of the mother liquors from, for instance, a mixture of ethanol and ether. A mixed melting-point between these two products showed a depression to about 140°C. Crystallisation of the mother liquors from a mixture of benzene and ether also yielded small traces of a compound melting at 237°C.

Wt.of IV (gm.)	Mol. of CLI	Solvent (ml.)	Catalyst	Conditions Time (hr.) and Temp.	Yield LXV (%)	Total Recovery of IV (%)
1·05	1·15	10, EtOH	1·1mol.Na	3, reflux	40	0
0·5	1·2	5, EtOH	1·33mol. Na.	12, cold	64	4
20·0	1·2	200, EtOH	1·33mol. Na.	20, cold	60	0
2·0	1·2	100, Et_2O	8 drops Et_2NH	100, cold	25	14
1·0	1·2	5, Et_2O	1 ml. Et_2NH	50, cold 120, reflux	40	36

Table X (continued overleaf)

Wt.of IV (gm.)	Mol. of CLI	Solvent (ml.)	Catalyst	Conditions (hr.)& Temp.	Yield LXV (%)	Total Recovery of IV (%)
1•0	3•0	25, Et_2O	0•5 ml. piperidine	40 days cold	64	0
2•5	3•0	75, Et_2O	1•25 ml. piperidine	60 days cold	14	0
1•2	1•2	100, EtOH	1•5ml. 20% aq Me_3N	7 days cold	0	79

Table X

Analysis of the compound M.P. 180-181•5°C.:-

Experimental Analysis: C 81•0% H 5•7%

Theory for $C_{25}H_{20}O_3$ (LXV): C 81•5% H 5•5%

Analysis of the compound M.P. 160-2°C.:-

Experimental Analysis: C 79•4% H 5•1%

Theory for $C_{25}H_{20}O_3$ (CLVI): C 81•5% H 5•5%

As separation of the principal reaction products by crystallisation was tedious and incomplete, chromatography was tried. An attempt to chromatograph 30 mg. of the mixed products on a 12" cellulose column that had been washed with water, butanol, and petrol-benzene mixture (4:1), using the last solvent mixture and toluene and butanol as eluents, gave no apparent separation. The use of an

alumina column was more successful as the high melting-point compound was eluted with the normal solvents, leaving most of the lower melting-point compound at the top of the column. This could then be eluted with acetone containing 1% of conc. HCl, and on neutralisation of the eluate with ammonia, evaporation, washing and crystallisation from acetone-ethanol, pale yellow crystals melting at 160-2°C. were obtained, which sublimed to form very fine pale yellow needles. This method of removal had the advantage that very little alumina was removed from the column.

It was found that the compound of M.P. 180-181·5°C. decolourised bromine in carbon tetrachloride solution extremely slowly, while the compound of M.P. 160-2°C. did not decolourise this. Ferric chloride in ethanol produced a slight yellow colour with a violet tinge with the compound melting at 180-181·5°C. and gave a distinct yellow orange colour with the compound melting at 160-2°C.

Attempted One Stage Wolff-Kishner[221,222] Reaction with 10-Phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene--12-one (LXV) using Hydrazine Hydrate (p. 112).

Two experiments were carried out as follows. 1·0 Gm. of LXV was dissolved in 15 ml. of ethylene glycol, and 1·0 ml. of hydrazine hydrate and 1·0 gm.

of KOH were added. The mixture was heated for two hours at 100°C. then boiled under reflux for a further hour, when the product was acidified, extracted with benzene or a mixture of benzene and ether, and washed to give a yellow solution with a blue green fluorescence in ultra-violet light. Addition of ether to the extract produced 0·7 gm. of a pale yellow crystalline powder of M.P. 215-230°C. A Lassaigne test proved the yellow powder to contain nitrogen, and therefore it could not be the desired 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene, CLXXVII, (see p.128 for possible pyrazolone structure CLXXV).[225]

Attempted Preparation of the Hydrazone of 10-Phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one, LXV, (p. 112).[129]

Two experiments were carried out as follows. 0·5 Gm. of LXV were dissolved in 20 ml. of benzene and 10 ml. of ethanol, and 10 ml. of hydrazine hydrate were added in two 5 ml. portions. The solution, which formed two layers, was then boiled under reflux for three hours. On crystallisation of the aqueous-alcoholic layer, yellow needles of M.P. 235-240°C. were obtained in 50% yield.

Attempted Wolff-Kishner Reaction with 10-Phenyl-11-carbethoxy-10:11:12:13:-tetrahydrofluoranthene-12-one (LXV) using the "Hydrazone" from the Previous Reaction (p.112).[221,222]

0·4 Gm. of the crude product from the above

experiment and 0·2 gm. of KOH were heated to 300°C. over 25 min. on a metal bath. After the solvent had been removed, the heating caused the solid residue to melt, and then to resolidify with the evolution of gas forming a reddish-black mass. When cool, the solid was ground up with a pestle and morter, acidified with HCl and extracted with a mixture of ether and chloroform. The extract was washed with water, dried, and crystallised with the addition of petrol giving a yellow powdery product of M.P. 225-235°C. which was shown by a Lassaigne test to contain nitrogen.

Attempted Wolff-Kishner Reaction with 10-Phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one (LXV) Using Semicarbazide Hydrochloride (p.112)[221,222,161]

In an attempt to prepare CLXXVI, the semicarbazone of LXV, 5 gm. of LXV were dissolved in 100 ml. of benzene, and a solution of 5 gm. of semicarbazide hydrochloride in 100 ml. of methanol and 20 ml. of saturated sodium acetate solution was added. The solution, which formed two layers, was heated overnight under reflux. The combined layers on crystallisation yielded 3·5 gm. of a yellow solid which melted at 250-260°C., apparently with decomposition.

The crude product was heated under reflux for 1½ hours with 1·0 gm. of sodium ethoxide in 30 ml. of ethylene glycol. An equal volume of water was then added and the solution was boiled under reflux for 30 min., diluted to 1·0 litres, filtered, acidified, and kept at 100°C. for a further hour.

A yellowish solid with a brilliant yellow ultra-violet fluorescence was obtained, M.P. about 220°C., which on recrystallisation from ethanol gave 0·6 gm. of a yellow powder melting at about 300°C. This product was found by a Lassaigne test to contain nitrogen and could not, therefore, be the expected 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydro-fluoranthene (CLXXVII) and was probably a pyrazo-lone derivative such as CXC (p. 128).

Attempted Clemmensen Reduction of 10-Phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one, LXV, (p. 111).[158,159,160]

0·2 Gm. of LXV, M.P. 178-180°C., and 2·0 gm. of amalgamated zinc were added to 3 ml. of conc. HCl, 2 ml. of toluene and 1 ml. of water and were boiled under reflux for 30 hours with the addition of three further 1 ml. portions of conc. HCl. When cool, the aqueous layer was diluted and separated from the toluene layer which was dried. Crystallisation of the toluene layer yielded unchanged starting material LXV, which was identified by mixed melting-point. No product corresponding to the expected 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene (CLXXVII) was obtained.

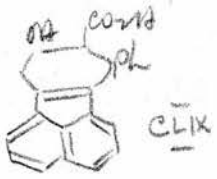
Reduction of 10-Phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one (LXV) with Potassium Borohydride (p. 112).[220,226]

Two experiments were carried out as follows. 3·0 Gm. of LXV in 100 ml. of dioxan were shaken for 20 hours in the cold with 2 gm. of powdered

potassium borohydride. The product mixture was extracted with sodium hydroxide solution, and the residue was washed with sodium bicarbonate solution and then water and dried to give a quantity of an oil which on crystallisation yielded 0.3 gm. of unchanged starting material LXV, M.P. 169-172°C., which was identified by mixed melting-point. The sodium hydroxide extract was acidified and extracted with ether, and the ethereal solution was extracted with sodium bicarbonate solution to separate it into acidic and phenolic fractions. The fraction containing acidic products, after acidification, washing and removal of solvent, yielded 1.0 gm. of an oil, believed to contain CLIX, which did not crystallise. The phenolic fraction yielded 0.2 gm. of an oil, believed to contain CLXV, which also did not crystallise.

Preparation and Dehydration of Oil Believed to Contain 10-Phenyl-11-carboxy-10:11:12:13-tetrahydrofluoranthene-12-ol, CLIX, (p. 112).

The oil from the previous experiment which was presumed to contain CLXV (as it was soluble in sodium hydroxide but not in sodium bicarbonate) was hydrolysed by dissolving it in sodium hydroxide and methanol and heating it at 90°C. for 1½ hours followed by standing overnight in the cold. The solution was extracted with ether, and the aqueous-methanolic portion was separated, acidified and extracted twice with ether, and this ether extracted was in turn extracted with sodium bicarbonate solution. Acidification of the last extract gave



an oily precipitate with a slight green fluorescence in ultra-violet light, which presumably contained CLIX.

0·2 Gm. of this oil were treated with phosphorus pentoxide for 2 hours in the cold, followed by 1½ hours under reflux. On elution with ether containing 10% of ethanol, this yielded a very small quantity of a yellow substance, M.P. 173-8°C., which had a green fluorescence in ultra-violet light.

In a second experiment, 1·0 gm. of the acidic product from the potassium borohydride reduction, believed to contain CLIX, was dissolved in 40 ml. of benzene and dried for 2½ hours with sodium sulphate. The solution was then dehydrated by refluxing for 2½ hours with 0·3 gm. of phosphorus pentoxide, a further two 0·3 gm. portions of phosphorus pentoxide being added during the reaction. Water was then added, and the product extracted with benzene. Crystallisation of this solution was not fruitful, and it was therefore chromatographed on alumina. Elution with benzene gave a pink colour on the column and a yellowish eluate with a green fluorescence in ultra-violet light, and a small quantity of a crystalline product was obtained, which after recrystallisation from acetone melted at 195-205°C. This was analysed.
Experimental Analysis; C 86·6% H 4·3%.
(For theoretical analyses, see Table VIII, p. 114).
Preparation of 10-Phenyl-9:10:11:12-tetrahydrofluoranthene-12-one, CLVII, (p. 115).

5·0 Gm. of 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one (LXV) were dissolved in 100ml. of glacial acetic acid, and 20 ml. of water containing 15 ml. of sulphuric acid were added and the mixture boiled under reflux for 2½ hours. 30 Ml. of water and 10 ml. of ethanol were added to the resulting orange solution, and it was allowed to crystallise, and deposited 2.5 gm. of crude product of M.P. 160-170°C. Recrystallisation of this from acetone yielded 1.8 gm. (45% of theory) of pale yellow crystals of M.P. 183-6°C. In an other experiment, an ether extract was made, purified by extraction with sodium bicarbonate solution and a 50% yield was obtained. Recrystallisation of the product from ethanol and acetone gave practically colourless crystals melting at 187-9°C., and analysis of these confirmed their identity as the expected 10-phenyl-9:10:11:12-tetrahydrofluoranthene-12-one (CLVII, see p. 115).

Experimental analysis: C 88.6% H 5.6%

Theory for $C_{22}H_{16}O$ (CLVII): C 89.2% H 5.4%

A specimen of this product was chromatographed on alumina to test whether it could be separated into an acenaphthylenic and an acenaphthenyl fraction (see p. 119). The compound gave a violet lake on the column, but did not separate. Working up of the mother liquors from the original crystallisations yielded a few milligrammes of a compound of M.P. 196-200°C.

Preparation of the 2:4-Dinitrophenylhydrazone of 10-Phenyl-9:10:11:12-tetrahydrofluoranthene-12-one, CLVII. (p. 115).[140]

50 Mg. of CLVII in 5 ml. of ethanol were treated with 5 ml. of 2:4-dinitrophenylhydrazine reagent (Allen's method[140]), heated to boiling, and three drops of HCl were added. After boiling for a further minute, a flesh coloured product crystallised out on cooling, and after recrystallisation from tetralin melted at 253-6°C. Further heating of the melt appeared to cause partial resolidification and remelting at 320-2°C., possibly caused by a bond shift.

Reduction of 10-Phenyl-9:10:11:12-tetrahydrofluoranthene-12-one (CLVII) with Potassium Borohydride[220,226] (p. 119).

1·6 Gm. of CLVII in 50 ml. of dioxan were heatedon a water-bath for 1½ hours with 0·5 gm. of potassium borohydride. The product was acidified, 20 ml. of water added, and it was kept overnight, but it did not crystallise. The solution was therefore separated into two layers with 50 ml. of NaOH solution, 50 ml. of methanol, 50 ml. of benzene and 20 ml. of water. The aqueous-methanolic portion was acidified, extracted with ether and the resulting solution, which had a green fluorescence in ultra-violet light, yielded crystals melting above 350°C. of boric acid. No other crystalline product was ontained.

Dehydrogenation of Oil from the Potassium Borohydride Reduction of 10-Phenyl-9:10:11:12-tetrahydrofluoranthene-12-one, CLVII, (p. 120).

0·5 Gm. of the oil from the previous experiment were dried, and heated up to 280°C. over a period of 30 min. with 0·2 gm. of 20% palladium on charcoal catalyst. The residues were extracted with benzene, petrol added, and a few impure yellow crystals of M.P. about 180°C. were obtained. The whole was therefore taken up in benzene and chromatographed on alumina. Elution with petrol gave a yellow solution with a blue-green fluorescence which deposited 20 mg. of pale yellow needles of M.P. 177-180°C. On crystallisation from petrol-benzene mixture, this product melted at 199-202°C., giving a viscous liquid which solidified on further heating and remelted at 321-3°C. On slow heating the compound did not appear to melt much ~~at all~~ at 199-202°C. Crystallisation of the mother liquors produced a few milligrammes of yellow needles, with a blue fluorescence in ultra-violet light, which meltedat 320-2°C. A mixture of the high and the low melting-point compounds started to melt at 199°C., not showing any depression in melting-point. A specimen of the compound of M.P. 199-202°C. after drying overnight was found to melt at 317-320°C., and analysis suggested its identity as the metaborate of 10-phenylfluoranthene-12-ol (CLXIV).

Experimental analysis: C 83·1% H 4·5% (12·4%)

Theory for $C_{22}H_{13}O_2B$ (CLXIV): C 82.5% H 4·1% O&B 13·4%

(See also Table IX, p. 121).

An attempt to work up 0·1 gm. of residues from this dehydrogenation by heating for 30min. at 560°C. with 0.3 gm. of palladium on charcoal catalyst gave no product.

Confirmation of the presence of borate in CLXIV (and hence also in CLXIII) was obtained by the development of a blue colour in the presence of para-nitrobenzene-azo-chromotropic acid reagent.[229]

Preparation of the 2:4-Dinitrophenylhydrazone of 10-Phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one, LXV, (p. 126).

60 Mg. of LXV were treated with 2:4-dinitrophenylhydrazine reagent by Allen's method.[140] After refluxing the solution overnight, a red crystalline compound was deposited, which was recrystallised from tetralin and melted at 246-7°C. An attempt to form the 2:4-dinitrophenylhydrazone by Brady's method[139,156] was unsuccessful and gave only a low melting-point product.

Experimental analysis: N 10·1%

Theory for 2:4-dinitrophenylhydrazone of LXV ($C_{31}H_{24}O_6N_4$): N 10·2%

Theory for pyrazolone of LXV ($C_{29}H_{18}O_5N_4$): N 11.2%

Attempted Hydrogenation of 10-Phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one, LXV, (p. 127).

25 Mg. of LXV were dissolved in 10 ml. of ethyl acetate and hydrogenated qualitatively in a Tower's microhydrogenator with Raney nickel as catalyst. Only unchanged starting material could be isolated at the end of the reaction.

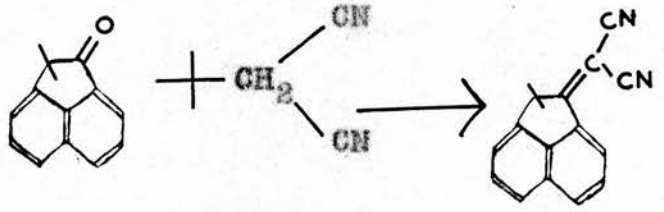
cf. 131

The Effect of Heating 10-Phenyl-11-carbethoxy-10:11-12:13-tetrahydrofluoranthene-12-one (LXV) with Sodium Ethoxide (p.144).

100 Mg. of LXV, M.P. 180-181.5°C., were dissolved in 5 ml. of absolute ethanol containing 0.1 gm. of sodium as its ethoxide. After heating for 14 hours at 100°C., the solution was crystallised from ethanol-acetone mixture to give 30 mg. of a product melting at 130-165°C. Chromatography of this yielded small quantities of unidentified crystals melting at about 115°C. and about 108°C., but no unchanged starting material.

Condensation of Acenaphthene-3-one (III) with Malononitrile, CXCVI, (p.132).

214,237,241,



III CXCVI CXCII

0.4 Gm. of malonitrile (CXCVI) and 1.0 gm. of acenaphthene-3-one (III) were dissolved in 18 ml. of benzene, and 0.14 gm. of sodium in 8 ml. of ethanol were added. After standing for 30 min.,

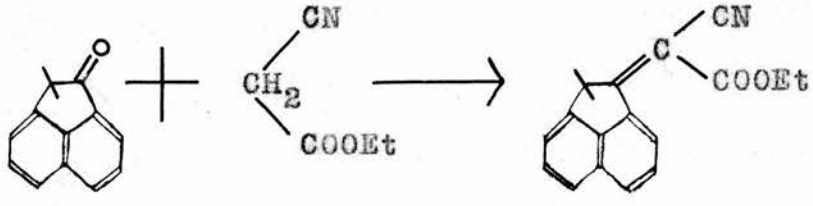
a further 0·14 gm. of sodium in 2 ml. of ethanol were added, and after 15 more min., water was added to the violet solution, which was extracted with a mixture of ether and petrol. The aqueous layer was recovered, washed, acidified with HCl and various attempts were made to purify the yellow precipitate, M.P. about 136°C., which was formed. The best product that was obtained by crystallisation from ethanol, benzene, nitrobenzene or glacial acetic acid, or by sublimation, formed birefringent lemon yellow needles, melting at 215-6°C., whose ethanolic solution gave a violet colouration with sodium hydroxide. Analysis of this compound did not accord well with the theory for acenaphthenylmalonitrile (CXCII), and the compound did not appear to be stable.

Experimental analysis: C 79·3% H 3·8%

Theory for $C_{15}H_8N_2$ (CXCII): C 83·3% H 3·7%

Attempts to catalyse the reaction with piperidine and with potassium ethoxide yielded only unidentified high melting-point products, while the ammonium acetate and acetic acid catalyst used by [214,237,241] Cope et alia for similar reactions yielded no product.

[214,239,241] Preparation of Acenaphthenylcyanoacetic Ester, (CXCIII) p. 133.



III CXCVII CXCIII

0·84 Gm. of acenaphthene-8-one (III) and 0·54 ml. of cyanoacetic ester (CXCVII) were added to 20 ml. of dry ethanol containing 0·11 gm. of sodium. A deep violet colour was immediately produced, and the solution was kept in the cold for 2 hours. Acidification with HCl yielded a yellow compound which crystallised from ethanol affording yellow crystals of M.P. 146·5-147·5°C. which gave a violet colouration with sodium hydroxide. The ultraviolet spectrum of this compound in dilute ethanolic HCl, in which it is stable, is shown on p. 136, and is quite different from its spectrum in alkaline-aqueous ethanol, in which, however, the compound is not stable.

Experimental analysis: C 77·4% H 4·7% N 5·2%

Theory for $C_{17}H_{13}O_2N$

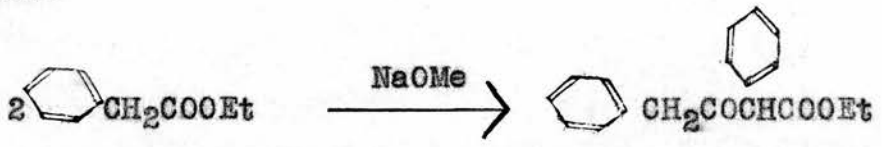
(CXCIII): C 77·6% H 5·0% N 5·3%

An attempt was made to condense cyanoacetic ester (CXCVII) with 7-benzylacenaphthene-8-one (CXCVIII) in the above manner, but analysis of the product showed it to contain no nitrogen.

Condensation of 7-Benzylideneacenaphthene-8-one with α:γ-Diphenylacetoacetic Ester

Preparation of α:γ-Diphenylacetoacetic Ester, CLXXXI, (p.138).

Phenylacetic ester was prepared by dissolving 40 gm. of phenylacetic acid in 200 ml. of ethanol and refluxing for 3 hours with 1·0 ml. of conc. sulphuric acid. Calcium carbonate was added to neutralise the sulphuric acid, and the calcium sulphate filtered off. The solvent was then removed and on distillation 36 gm. of ester were obtained.



CLII CLXXXI

13 Gm. of phenylacetic ester (CLII) were heated on a water-bath for 30 min. with 1·8 gm. of sodium as its methoxide. Addition of petrol and ether caused the deposition of 3·5 gm. of crude crystalline α:γ-diphenylacetoacetic ester (CLXXXI) of M.P. 70°C. (Lit. M.P.77-78°C.).
[215,224]

Condensation of α:γ-Diphenylacetoacetic Ester (CLXXXI) with 7-Benzylideneacenaphthene-8-one, IV, (p.138).
[51]

0.07 Gm. of sodium were dissolved in 30 ml. of absolute ethanol, and 0·7 gm. of the ester (CLXXXI) were added, followed by 0·5 gm. of the ketone (IV)

dissolved in 5ml. of absolute ethanol. A red colour developed and the solution was kept in the cold overnight. The solution was then acidified with glacial acetic acid until it turned yellow, and on evaporation and cooling deposited 0·5 gm. of crude product as very pale yellow crystals of M.P. about 190°C. Recrystallisation of this substance from ethanol, followed by sublimation and further crystallisation, gave colourless monoclinic crystals of M.P. 202-3°C. Working up of the mother liquors of the crude reaction product with ethanol yielded 0·2 gm. of colourless crystals of M.P. 200-235°C. Sublimation of the latter, followed by crystallisation from chloroform-ether mixture, yielded colourless tetragonal crystals of M.P. 247-250°C. Neither product was soluble in sodium carbonate solution.

Analysis of compound of M.P. 202-3°C.:-

Experimental analysis:	C 83·4%	H 4·4%

Analysis of compound of M.P. 247-250°C.:-

Experimental analysis:	C 81·8%	H 4·8%
Theory for $C_{37}H_{30}O_4$ (CLXXXII):	C 82.5%	H 5·6%
Theory for $C_{37}H_{28}O_3$ (CLXXXIII):	C 85·4%	H 5·4%
Theory for $C_{27}H_{20}O_3$ (CLXXXV):	C 82·6%	H 5·1%

Condensation of 7-Benzylideneacenaphthene-8-one with sym-Tetraphenylacetone

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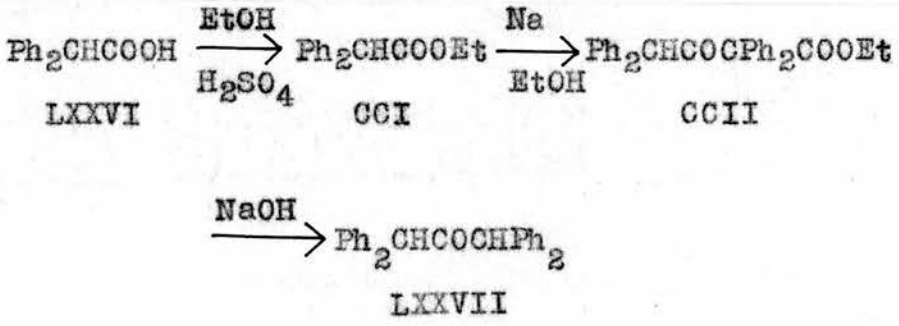
Preparation of sym-Tetraphenylacetone, LXXVII, (p.141).

Sym-tetraphenylacetone (LXXVII) was prepared by the method indicated in Scheme W;



LXXVI CCI CCII LXXVII

Scheme W

The diphenylacetic ester (CCI) was prepared by boiling 6 gm. of diphenylacetic acid (LXXVI) for 3 hours with 20 ml. of ethanol containing 3 drops of conc. H_2SO_4. After neutralisation and distillation, the product was crystallised from petrol and melted at 56-7°C. (Lit. 58°C.).

4 Gm. of diphenylacetic ester (CCI) in 40 ml. of ether were treated with 0·66 gm. of sodium slices and kept in the cold for 4 days. The solution was cooled in ice, and ethanol added over a period of 30 min. to destroy any remaining sodium, whereafter 30 ml. of water were added and the α:α:γ:γ-tetraphenylacetoacetic ester (CCII) was extracted with ether and washed successively with water and 33 ml. of 5% sodium bicarbonate solution.

After removal of the ether, the ester (CCII) was hydrolysed by treatment with 8 ml. of 5% NaOH. The product was steam distilled to remove impurity, and was crystallised from a mixture of ether and petrol giving 0·7 gm. of impure sym-tetraphenylacetone (LXXVII) of indefinite melting-point.

Condensation of sym-Tetraphenylacetone (LXXVII) with 7-Benzylideneacenaphthene-8-one (IV) using Sodium Ethoxide as Catalyst (p.141[215,224]).

Sodium (0·1 gm.) was dissolved in 10 ml. of ethanol and 0·5 gm. of sym-tetraphenylacetone (LXXVII) were added, followed quickly by a solution of 1·0 gm. of IV in 10 ml. of ethanol. The solution was warmed to redissolve the IV which crystallised out, kept standing for 2 hours, and became red in colour. 7-Benzylideneacenaphthene-8-one (IV) crystallised out and the reaction mixture was therefore boiled for 3 hours before acidification with glacial acetic acid, washing and extraction with ether. Charcoal treatment and evaporation of the extract gave no crystalline product.

The solution was therefore chromatographed from benzene on alumina, yielding 0·2 gm. of diphenyl-acetic acid (LXXVI), M.P. 148-9°C., and 15 mg. of 10:15-diphenyl-11:12-benzfluoranthene (LXIV), M.P. 260°C. The identities of these products were confirmed by mixed melting-point determinations.

In view of the possibility of the dehydration of the initial condensate CC being incomplete, all

the residues were combined, dried, treated in ether with dry HCl, washed successively with water, sodium carbonate solution and water, and then redried. Chromatography of the resulting solution yielded, presumably by simple purification, a further 30 mg. of 10:13-diphenyl-11:12-benzfluoranthene (LXIV). No further pure product was isolated from the reaction.

Condensation of sym-Tetraphenylacetone (LXXVII) with 7-Benzylideneacenaphthene-8-one (IV) Using Piperidine[208,218,224] and Catalytic Quantities of Sodium Ethoxide[209] as Catalyst (p.142).

0·6 Gm. of LXXVII and 0·4 gm. of IV were dissolved in 10 ml. of ethanol and 2 drops of 1% sodium ethoxide[209] in ethanol were added (Kohler's method). No reaction appeared to occur with this catalyst, and 4 drops of piperidine were therefore added[208,218,224] (Knoevenagel's method) and the solution boiled under reflux for 5½ hours during which time it darkened slightly. After acidification of the reaction mixture with glacial acetic acid and crystallisation from ethanol, 0·2 gm. of unchanged 7-benzylideneacenaphthene-8-one (IV) were obtained, but no other product. The solvent was therefore removed and the reaction product chromatographed on alumina from benzene-petrol mixture yielding a further 0·15 gm. of unchanged 7-benzylideneacenaphthene-8-one (a total of 87·5% recovery) along with a blue fluorescent solution, eluted with petrol, which presumably contained a small quantity

of 10:13-diphenyl-11:12-benzfluoranthene (LXIV). The recovered starting material was identified by mixed melting-point.

Section V

The Preparation and Properties of the Ketochloride of 7-Benzylideneacenaphthene-8-one

The Preparation of the Ketochloride (CCVIII)[230,234] of 7-Benzylideneacenaphthene-8-one[81]. IV. (p.147).

The method followed was based on that of Straus[230], and the following variation was found to give the best results. 2·2 Gm. of dry recrystallised IV were dissolved in 15 ml. of dry benzene and treated at the boiling-point with 1.8 gm. of phosphorus pentachloride, this being added in two portions. The resulting mixture was heated until the PCl_5 had dissolved and thereafter for 30 min. The solution, once cool, was washed successively with water, sodium bicarbonate solution and twice again with water, and was then dried with calcium chloride. In the presence of fresh solid calcium chloride, the solution was saturated with dry hydrogen chloride (with cooling) and kept overnight after sucking off most of the HCl.

The solution was concentrated under vacuum and yielded, on addition of benzene-petrol mixture, 0.6 gm. of starting material (IV), which was filtered off. The mother liquors were worked up by cooling their light petroleum-ether solution in

solid carbon dioxide and yielded 0·5 gm. of ill defined yellow crystals of M.P. 72°C.

Analysis of the crude product and the production with conc. sulphuric acid of the red-violet colour typical of 'ketochlorides' confirmed that this compound was 7-(α-chlorobenzyl)-8-chloroacenaphthylene (CCVIII), the ketochloride of 7-benzylideneacenaphthene-8-one (IV).

Analysis of the crude ketochloride, M.P. 72°C,:-

Experimental Analysis: Cl 21·2%

Theory for $C_{19}H_{12}Cl_2$ (CCVIII): Cl 22·8%

A small quantity of a yellow crystalline chloro compound of M.P. 256-7°C. was also obtained from the crystallisation from light petroleum-ether mixture, and was recrystallised from chloroform. The molecular weight of this compound was found to be 526, suggesting that it was dimeric.

Methylation of the Ketochloride (CCVIII) of 7-Benzylideneacenaphthene-8-one, IV, (p. 148).[230,232]

This methylation was attempted in two stages in accordance with the literature,[230] but in practice only the expected product of the first stage, LXIX, was obtained (see Scheme Z, p. 148).

Uncrystallised ketochloride prepared from 2·6 gm. of IV was dissolved in a little ether and 40 ml. of methanol, and treated with 14 ml. of 1% methanolic sodium methoxide (equivalent to ½% sodium in methanol). The solution was then evaporated down at the water-pump, a further 14 ml. of

1% sodium in methanol were added and the whole was boiled under reflux for 60 hours. The colour of the solution darkened slightly, and the production of a crimson colour with conc. sulphuric acid showed that no ketochloride remained. The solution was therefore evaporated and distilled, using apparatus of the type shown on p. 181, to yield 0·4 gm. of a yellow oil which crystallised from ether-ethanol mixture in bright yellow leaflets of M.P. 60-61·5°C. Analysis showed this compound to be 7-(w-methoxybenzyl)-8-chloroacenaphthylene (LXIX) instead of the expected 7-benzoylacenaphthylene (CCIV).

Experimental Analysis: C 77·6% H 5·0% Cl 11·8%

Theory for $C_{20}H_{15}OCl$ (LXIX): C 78·3% H 4·9% Cl 11·6%

Theory for $C_{19}H_{12}O$ (CCIV): C 89·0% H 4·7% Cl 0·0%

Attempts were made to force the methylation of the remaining chlorine atom in LXIX using 2% sodium in methanol (60 hr. reflux), 10% sodium in methanol (5 hr. reflux) and 2% potassium in methanol (4½ hr. reflux) but all yielded unchanged starting material, and no other solid was isolated.

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Hydrolysis of 7-(w-Methoxybenzyl)-8-chloroacenaphthylene, LXIX, (p.147).

10 Mg. of crystalline LXIX were heated for five minutes in 5 ml. of methanol containing two drops of conc. sulphuric acid, and on cooling, pale

yellow laminar crystals were formed, M.P. 114°C., which gave no depression in melting-point when mixed with a specimen of 7-benzylideneacenaphthene-8-one (IV, M.P. 117°C.). The hydrolysis was repeated varying the conditions, using 50% HCl in methanol and refluxing for various periods up to three hours. In each case the same product was obtained.

Preparation of a 2:4-Dinitrophenylhydrazone from 7-(w-Methoxybenzyl)-8-chloroacenaphthylene, LXIX, (p. 148).[140]

50 Mg. of LXIX were dissolved in 5 ml. of ethanol and 5 ml. of a solution of 2:4-dinitrophenylhydrazine were added. The solution was then boiled under reflux for a short time in the presence of three drops of conc. HCl (Allen's method[140]) which would be expected to hydrolyse the LXIX to form 7-benzylideneacenaphthene-8-one (IV). A 2:4-dinitrophenylhydrazone was formed which after crystallisation from toluene melted at 244-5°C. (with decomposition) and corresponded in melting-point and analysis with the 2:4-dinitrophenylhydrazone of 7-benzylideneacenaphthene-8-one (M.P. 242-4°C., with decomposition.).

Experimental Analyses: N 11·9% & 12·2%

Theory for $C_{25}H_{16}O_4N_4$: N 12·8%

Preparation of Chalkone (XVI) and Cinnamylideneacetophenone, CCV, (p. 148).[233,235]

The method used was that of Claisen[233,235]

Preparation and Methylation of the Ketochlorides of Chalkone (XVI) and Cinnamylideneacetophenone (CCV)[230,231,232,234], and the Hydrolysis of the Methylated Products (p. 148).

These experiments were carried out exactly in accordance with the method given by Straus[231] for the preparation of the ketochloride of cinnamylideneacetophenone, and by the method given by Straus and Blankenhorn[232] for the methylation of the ketochloride. The hydrolyses were likewise carried out by the methods described by the above authors, and the regenerated starting materials were isolated by crystallisation and were identified by mixed melting-point determinations.

Preparation of 7-Cinnamylideneacenaphthene-8-one, CLXX, (p. 149).

3·0 Gm. of acenaphthene-8-one (III) and 9 ml. of crude cinnamaldehyde were dissolved in 250 ml. of absolute ethanol. Alkali was added dropwise until the solution became red, then it was kept at room temperature for 60 hours and 1·2 gm. (24% of theory) of a yellow crystalline product of M.P. 164-5°C. were obtained. Recrystallisation from ethanol gave a melting-point of 165-6°C. The ultra-violet spectrum of this compound is shown on p. 161 .

Experimental Analysis: C 88·7% H 5·3%

Theory for $C_{21}H_{14}O$ (CLXX): C 89·3% H 5·0%

Preparation of the Ketochloride (CCIX) of 7-Cinnamylideneacenaphthene-8-one, CLXX, (p. 149).

A boiling solution of 1·0 gm. of 7-cinnamylideneacenaphthene-8-one (CLXX) in 10 ml. of dry benzene was treated with 0·8 gm. of PCl_5, this being added in two portions. When all the PCl_5 had dissolved (30 min.), the solution was boiled for a further 10 min., cooled, poured into ice-water, shaken with water, and washed successively with sodium bicarbonate solution and water. The solution was then dried with calcium chloride, decanted, redried, saturated with dry hydrogen chloride in the presence of calcium chloride and kept overnight. The presence of the ketochloride CCIX in solution was shown by the typical violet colour produced with conc. sulphuric acid, but evaporation of the solution under reduced pressure did not yield a crystalline product.

Section 6

Attempted Diene Reactions with 7-Benzylideneacenaphthene-8-one and Chalkone

Attempted Diene Reaction between Vinyl Butyl Ether (CXIX)[51] and 7-Benzylideneacenaphthene-8-one, IV, (p. 151).[175]

1·5 Ml. of CXIX were placed in an open phial at the bottom of a test-tube and 1 gm. of IV, along with 1·3 mg. of hydroquinone as antioxidant were placed in the test-tube around and on top of the phial, and the test-tube was then stoppered with glass-wool. The test-tube was placed inside a Carius tube which was sealed after flushing out with nitrogen. In two separate experiments, two Carius tubes were prepared in this way and were heated in an autoclave for 16 hours at 190°C. and 225°C., respectively.

A yellow-brown tarry solid was produced by the reactions, from which no pure product was isolated except a small quantity of unchanged IV from the reaction at 190°C.

Preparation of 1-Benzylidenecyclohexane-2-one,[77] CXVII, (p. 152).[175]

88 Gm. of cyclohexanone, 18 gm. of NaOH and 32 gm. of benzaldehyde were stirred in 4·16 litres

of water at room temperature for 12 hours, whereafter the solution was neutralised with 25 ml. of glacial acetic acid. The mixture was then extracted three times with benzene and the benzene extract, after washing and filtering, was distilled under reduced pressure to give 7 gm. (12·5% of theory) of 1-benzylidenecyclohexane-2-one (CXVII) of M.P. 51-3°C. (lit. 51-3°C.).

Preparation of 2-Butoxy-3:4:5:6:7:8-hexahydro-4-phenyl-2H-benzopyran, CXXII, (p.152).[175] [177]

1 Gm. of 1-benzylidenecyclohexane-2-one (CXVII) and 1·5 ml. of vinyl butyl ether (CXIX) were mixed in 10 ml. of dry ether, and 10 drops of BF_3 in glacial acetic acid were added and dissolved with the help of 2 ml. of glacial acetic acid. The solution, which immediately became warm, was left overnight in the refrigerator. The solution became a flourescent red colour and a few red needles, which had deposited and which melted with decomposition at about 200°C., were filtered off. The solution was neutralised with NaOH and after the removal of solvent was distilled in high vacuum to give 0·8 gm. of a yellow oil, B.P. 105-110°C./0·3 mm. (52% of theory), followed by 0·4 gm. of a red brown oil, B.P. 250-270°C./0·1 mm. The principal product was redistilled to give a yellow oil, B.P. 180-186°C./1 mm., which was analysed.

The boiling-point of the product believed to be CXXII was of the same order as that of 2-ethoxy-3:4:5:6:7:8-hexahydro-4-phenyl-2H-benzopyran

(CXVIII), BP. 160-2°C./4 mm., and the refractive indices of the compounds were close (n^{25} of CXXII was 1·5694, lit. n_D^{25} of CXVIII is 1·5346). The analysis of the product confirmedits identity as CXXII.

Experimental analysis: C 79·9% H 8·5%

Theory for $C_{19}H_{26}O_2$ (CXXII): C 79·7% H 9·2%

Attempted Diene Reaction with Vinyl Butyl Ether (CXIX) and 7-Benzylideneacenaphthene-8-one[51] (IV) Using a BF_3 Catalyst (p. 152).

Several attempts were made to obtain reaction with CXIX and IV by mixing them in the presence of BF_3 catalyst (in glacial acetic acid) and a suitable dried solvent. The reaction was attempted under various conditions which are summarised in Table XII below:-

Quantity of CXIX (ml.)	Quantity of IV (gm.)	Quantity of BF_3 in HOAc	Solvent	Quantity of solvent (ml.)	Temp. (°C.)	Time (hr.)
0·15	0·12	3 ml. of 1% sol.in HOAc	HOAc	100	Room temp.	17
0·15	0·12	2 drops	HOAc	100	25 100	2/3 1/2
0·15	0·1	2 drops	Ether	50	Room temp	20
1·0	0·1	10 drops	Ether	25	"	16
0·5	1·0	4 drops	Benzene	20	30-40	3
0·3	0·2	2 drops	" & HOAc	20 & 10	0	384

Table XII

In no case was any product isolated from the reaction other than unchanged starting material.

Attempted Diene Reaction with Diphenylketene (XLII)[129-131] and 7-Benzylideneacenaphthene-8-one (IV)[51] Using a BF_3 Catalyst (p. 153).

Two attempts were made to carry out this reaction. In the first, 5 gm. of IV and 4 gm. of XLII were dissolved in 10 ml. of benzene and allowed to stand with 5 drops of BF_3 catalyst (in glacial acetic acid) for two hours at room temperature under nitrogen. In the second, 1 gm. of IV and 0·8 ml. of XLII were dissolved in a little glacial acetic acid, 1 ml. of a 10% glacial acetic acid solution of BF_3 catalyst (in glacial acetic acid) was added and the solution was heated at 100-130°C. for 1 hour. In both cases, working up yielded only unchanged IV (44% and 55% respectively) and diphenylacetic acid, both of which were identified by mixed melting-point.

Attempted Diene Reaction with Diphenylketene (XLII)[129-131] and Chalkone (XVI) Using a BF_3 Catalyst (p. 153).

4 Gm. of XVI and 4 gm. of XLII were dissolved in 10 ml. of benzene, 5 drops of BF_3 catalyst (in glacial acetic acid) were added and the mixture was kept for two hours under nitrogen in the cold. Working up yielded only unchanged XVI (85%) and diphenylacetic acid, the identities of which were proved by mixed melting-point.

Reaction between Chalkone(XVI) and Ketene (CIX) in the Presence of BF_3 Catalyst (p.153).[170,171,174,176]

5 Gm. of XVI were heated to 100°C. and 3 drops of BF_3 catalyst (in glacial acetic acid) were added. The melt was maintained at 100-110°C. for 13 min. and ketene (p. 203) passed over it. A bright red colour was rapidly developed which dissolved in phosphoric acid when the melt was taken up in phosphoric acid-petrol-ether mixture. The red compound was found to be soluble in dioxan, acetone, chloroform and ethylene dichloride as well as in phosphoric acid, and gave red solutions. The petrol layer from the initial extraction yielded 0·2 gm. of unchanged XVI, but no other pure solid was obtained.

Attempted Diene Reaction between Acetylene and 7-Benzylideneacenaphthene-8-one (IV) in the Presence of BF_3 Catalyst (p. 156).

The ketone (IV, 0·1 gm.) was dissolved in 10ml. of dry benzene, two drops of BF_3 in glacial acetic acid were added and dry acetone-free acetylene was bubbled through the solution. 0·7Gm. (70%) of unchanged IV was the only reaction product.

Section VII

Some Reactions of 7-Benzylidene- and 7-(ortho-Bromobenzylidene)-acenaphthene-8-one

Reduction and Hydrogenation of 7-Benzylideneacenaphthene-8-one

Attempted Hydrogenation of 7-Benzylideneacenaphthene-8-one (IV) with Raney Nickel as Catalyst (p. 157).

One gm. of 7-benzylideneacenaphthene-8-one (IV) in 70 ml. of absolute ethanol was shaken with hydrogen under 1½ atmospheres pressure for one hour in the presence of a small quantity of Raney nickel as catalyst. The solution became colourless (it darkened slightly in air) but no crystalline product was obtained either directly or after chromatography. It was thought that the inability to obtain a crystalline product might be due to the presence of the isomers of 7-benzylacenaphthene-8-ol (CCXIII), and the residues were therefore heated in sulphur free xylene with anhydrous $KHSO_4$ in the hope of forming 7-benzylacenaphthylene (CXCIV), but again no crystalline product was obtained.

158-160
Attempted Clemmensen Reduction of 7-Benzylideneacenaphthene-8-one (IV), p. 157 .

Two gm. of zinc foil were cleaned and amalgamated then placed in a flask with 2 ml. of water, 6 ml. of conc. HCl, 3 ml. of toluene and 1 gm. of the ketone (IV). The solution was boiled under reflux for 30 hours with four further additions at 6 hourly intervals of 2 ml. of conc. HCl. After cooling and dilution, an ether extract of the dark coloured solution was prepared and dried, and a small quantity of a substance which sublimed at 325°C. to form long yellow plates melting above 350°C. was obtained. No further pure product was isolated either by direct crystallisation or after chromatography.

Attempted Reduction of 7-Benzylideneacenaphthene-8-
246
one (IV) with Zinc and Acetic Acid (p. 158).

One gm. of 7-benzylideneacenaphthene-8-one (IV) in a mixture of 8.5 ml. of glacial acetic acid, 8.5 ml. of ether and 0.2 ml. of water was cooled in freezing mixture and treated over a period of 3 min. with 1.0 gm. of zinc dust. The mixture was then shaken in freezing mixture for a further 3 min. The reactants were next poured into a mixture of 4.7 ml. of ether and 17.0 ml. of petrol, and the product quickly washed with ice-water till free of zinc and most of the acetic acid. The ether was removed by a stream of CO_2, still keeping the temperature below 0°C., and on addition of

petrol a crude crystalline product was obtained. Separation and crystallisation of this with ether and petrol afforded 0·1 gm. of a substance which when purified meltedat 229-232°C., along with a small quantity of unchanged 7-benzylideneacenaphthene-8-one (IV), identified by mixed melting-point determination, and a few unidentified yellow crystals melting at 258-260°C. The compound of melting-point 229-232°C. was shown by a mixed melting-point determination to be the same as one of the substances obtained from the hydrogenations of IV with PtO_2 and Raney nickel catalysts (p. 252).

Meerwein-Ponndorf Reduction of 7-Benzylideneacenaphthene-8-one, IV, (p. 158).

To prepare the aluminium isopropoxide reagent, 13·7 gm. of aluminium foil and 150 ml. of dry isopropanol were treated with 0·25 gm. of mercuric chloride, warmed and 1 ml. of carbon tetrachloride was added. The warming was continued till the reaction became vigorous, when cooling was applied to control it, and finally the reactants were boiled overnight. The resulting reagent was filtered and diluted with 500 ml. of isopropanol.

One gm. of 7-benzylideneacenaphthene-8-one (IV) was dissolved in 6 ml. of aluminium isopropoxide reagent and the resulting solution distilled on a water-bath using a Hahn condenser. As soon as the acetone test showed the quantity of acetone present in the distillate to be very small, the isopropanol was distilled off, the residue dissolved in ether and extracted twice with a 20% aqueous

solution of HCl. The ether extract was washed with water, petrol was added and an oil which did not crystallise was obtained. A further attempt was made to reduce this oil (with red phosphorus and iodine, see p. 251), but no product was obtained. A small quantity of very fine colourless needles melting at 95-6°C. was obtained from the mother liquors of this oil along with small quantities of impure products melting at about 148°C. and 171°C. It was presumed from the specific nature of this reduction that the compound melting at 95-6°C. must be the expected 7-benzylideneacenaphthene-8-ol (CCXII), though its analysis did not closely support this.

Experimental analysis: C 86·3% H 5·04%

Theory for $C_{19}H_{14}O$ (CCXII); C 88·3% H 5·46%

Attempted Reduction of 7-Benzylideneacenaphthene-8-one (IV) with Lithium Aluminium Hydride (p. 158).

Lithium aluminium hydride (0·1 gm., in 3 ml. of dry ether) was placed in a flask from which moisture was excluded and the ketone (IV, 0·5 gm.) in 5 ml. of ether was added at such a rate as gave gentle ebullition of the ethereal solution in the flask. A red suspension was formed, and 10 min. after the final addition a few drops of water were cautiously added. The reaction mixture was then poured into 1 ml. of ice-water and 2 ml. of 10% H_2SO_4 were added. The oil was extracted with ether but attempts to crystallise it from ethanol were unsuccessful, and a further attempt to reduce

the oil with red phosphorus and iodine was made (see below).

Attempted Reduction of Oils from Lithium Aluminium Hydride and Meerwein-Ponndorf Reductions of 7-Benzylideneacenaphthene-8-one (IV), using Red Phosphorus and Iodine (p. 158).

2.0 Gm. of oil from the above Meerwein-Ponndorf and lithium aluminium hydride reductions of IV were dissolved in 60 ml. of glacial acetic acid and 6 ml. of water and boiled under reflux for 3 hours with 2 gm. of red phosphorus and 2 gm. of iodine. Attempts were made to crystallise and distil the product, but no pure substance was isolated.

Wolff-Kishner Reduction of 7-Benzylideneacenaphthene-8-one (IV), p. 158.

One gm. of 7-benzylideneacenaphthene-8-one (IV, in 20 ml. of ethylene glycol), 0·5 ml. of hydrazine hydrate and 1·0 gm. of potassium hydroxide were heated for 30 min. at 100°C. then under reflux for 30 min. Acidification, ether extraction and crystallisation from petrol afforded 0·15 gm. of colourless platelets of M.P. 149-150°C., the analysis of which confirmed their identity as 7-benzylideneacenaphthene (CCXIV).

Experimental analysis: C 94·1% H 6·0%

Theory for $C_{19}H_{14}$ (CCXIV): C 94·2% H 5·8%

Attempts to perform the reaction by isolation of the hydrazone and treatment of this with

potassium hydroxide gave only traces of product. The compound presumed to be the hydrazone, prepared by refluxing IV in ethanol with excess hydrazine hydrate, yielded brownish yellow prisms melting at 229-230°C. after crystallisation from ethyl acetate. Analysis of this compound did not accord well with the composition of the hydrazone.

Experimental analysis: N 8·3%

Theory for hydrazone of IV ($C_{19}H_{14}N_2$): N 10·4%

Hydrogenation of 7-Benzylideneacenaphthene-8-one (IV) with Adam's PtO_2 Catalyst (p.159).

One gm. of 7-benzylideneacenaphthene-8-one (IV) in 200 ml. of ethyl acetate was shaken with hydrogen at room temperature under one atmosphere pressure in the presence of 5 mg. of Adam's PtO_2 catalyst. After four hours, the yellow colour of the solution became pale and as nearly the theoretical uptake of hydrogen had been reached, the catalyst was removed. The solution was evaporated and crystallised to give 0·65 gm. of crude 7-benzylacenaphthene-8-one (CXCVIII) which when recrystallised from ethanol afforded birefringent colourless plates melting at 81-2°C. 0·07 Gm. of a compound which crystallised from chloroform to form birefringent colourless plates melting at 234-6°C. were also obtained from this reaction. The analysis of the compound melting at 81-2°C. confirmed its identity as 7-benzylacenaphthene-8-one (CXCVIII), but that of the compound melting at 234-6°C. suggested that the high melting-point compound contained

a larger proportion of oxygen and it was assumed to be a dimeric product and remained unidentified. This latter compound was shown by a mixed melting-point determination to be identical with the unidentified product of the reduction of IV with zinc and acetic acid (p.248).

Analysis of the compound melting at 81-2°C.:-

Experimental analysis: C 88·0% H 5.4%

Theory for $C_{19}H_{14}O$ (CXCVIII): C 88·3% H 5·5%

Analysis of compound melting at 234-6°C.:-

Experimental analyses: C 85·6% H 4·7%

C 85·1% H 5·3%

The ultra-violet spectrum of CXCVIII is shown on p. 162.

Preparation of the 2:4-Dinitrophenylhydrazone of 7-Benzylacenaphthene-8-one, CXCVIII, (p. 158).

The 2:4-dinitrophenylhydrazone was prepared by Allen's[140] method and formed yellow needles which were crystallised from toluene and tetralin to give a melting-point of 230·5-232°C.

Experimental analysis: N 11·9%

Theory for 2:4-dinitrophenylhydrazone of CXCVIII ($C_{25}H_{18}N_4O_4$): N 12·8%

7-Benzylacenaphthene-8-one (CXCVIII) was found to slowly decolourise bromine in carbon tetrachloride solution and gave a slight yellow orange colour with ferric chloride in ethanolic solution.

Hydrogenation of 7-Benzylideneacenaphthene-8-one (IV) Using Raney Nickel in the Presence of HCl as Catalyst (p. 158).[244]

1.13 Gm. of 7-benzylideneacenaphthene-8-one (IV) in 100 ml. of ethanol were hydrogenated using 5 gm. of freshly prepared Raney nickel catalyst (made from 10 gm. of a 1:1 nickel-aluminium alloy) in the presence of 0·28 ml. of conc. HCl to inhibit the reduction of the carbonyl group.[244] Hydrogen was quickly absorbed and after 1½ hours the nearly colourless solution was filtered through a sintered glass filter. Crystallisation from ethanol afforded 1 gm. (99% of theory) of 7-benzylacenaphthene-8-one (CXCVIII).

The α:β-Unsaturated Properties of 7-Benzylideneacenaphthene-8-one

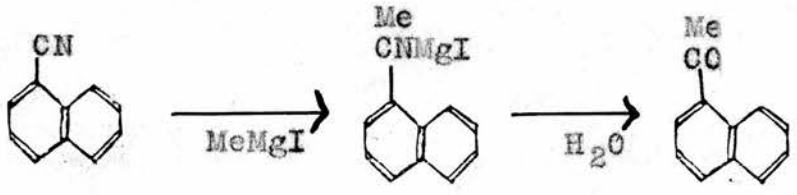
Preparation of the 2:4-Dinitrophenylhydrazone of 7-Benzylideneacenaphthene-8-one, IV, (p. 160).[140]

The 2:4-dinitrophenylhydrazone of 7-benzylideneacenaphthene-8-one (IV) was prepared by Allen's[140] method and formed very fine red needles which crystallised from tetralin or benzene and melted at 242-4°C. (with decomposition). No analysis of this compound was made, but its ultra-violet spectrum is shown on p. 256.

7-Benzylideneacenaphthene-8-one (IV) was found to decolourise bromine dissolved in carbon tetrachloride very slowly, and it gave a very slight yellow colour with ferric chloride solution in ethanol.

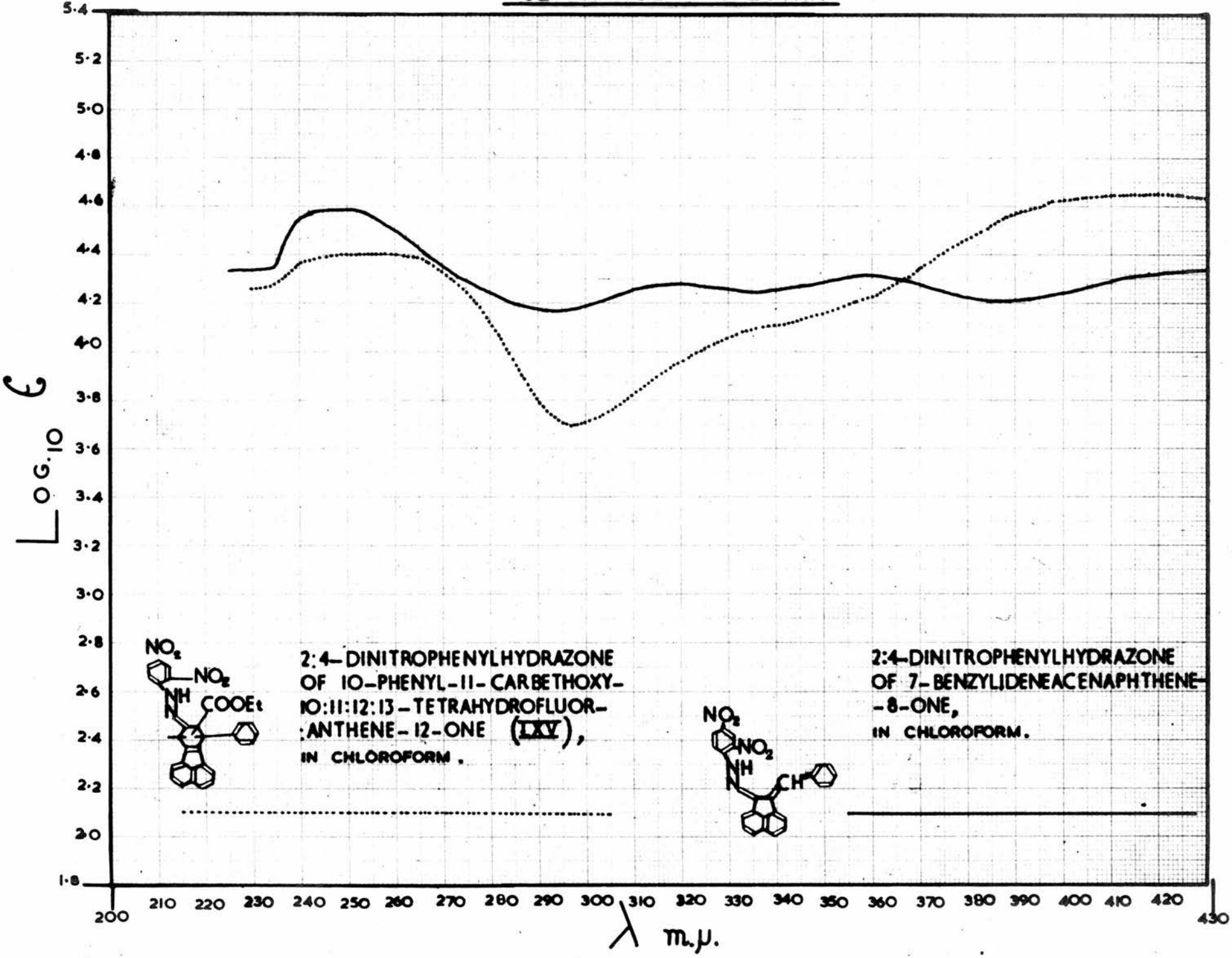
Preparation of α-Acetylnaphthalene, CCXVI, (p.160).[247-249]

α-Acetylnaphthalene (CCXVI) was initially prepared by the action of methylmagnesium iodide on α-cyanonaphthalene (CCXVII, 7·7 gm.), but the product obtained was not pure enough for spectroscopic purposes. The preparation was therefore



CCXVII CCXVI

ULTRA-VIOLET SPECTRA

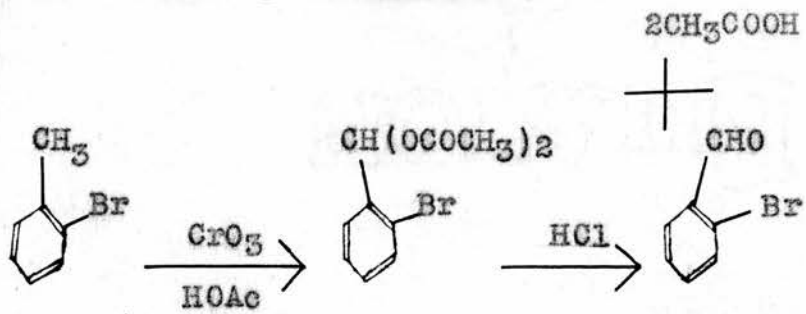


carriedout by the action of acetyl chloride on naphthalene in the presence of aluminium chloride using ethylene dichloride as solvent.[247] After purification of the product by the formation and decomposition of its picrate,[249] colourless crystals were obtained melting at 10.5°C. (lit.[249] 10·5°C.), and the ultra-violet spectrum of the compound was observed (p. 162).

Preparation and Attempted Ring-Closure of 7-(ortho-Bromobenzylidene)-acenaphthene-8-one

Preparation of ortho-Bromobenzaldehyde, CCXVIII, (p.166).[251,252]

The preparation of ortho-bromobenzaldehyde (CCXVIII) was tried by direct bromination of benzaldehyde under ultra-violet light,[251] but only small yields were obtained along with large quantities of by-products. The method of Brady and Casson[252] was therefore used and gave better yields. By this method, ortho-bromotoluene (CCXIX) in solution in glacial acetic acid, acetic anhydride and sulphuric acid was oxidised with chromic anhydride and yielded the diacetate of ortho-bromobenzaldehyde (CCXX), which was hydrolysed with conc. HCl to form ortho-bromobenzaldehyde (CCXVIII).



CCXIX CCXX CCXVIII

Preparation of 7-(ortho-Bromobenzylidene)-acenaphthene-8-one, CCX, (p. 166).[51]

0.15 Gm. of ortho-bromobenzaldehyde (CCXVIII) and 0.25 gm. of acenaphthene-8-one (III) were diss-

olved in 30 ml. of ethanol. and a few drops of sodium hydroxide solution were added. The solution was kept standing over the weekend and yielded, after recrystallisation from ethanol, 50 mg. of yellow needles of 7-(ortho-bromobenzylidene)-acenaphthene-8-one (CCX) melting at 143-5°C. A quantity of a compound melting at 208-216°C., which was believed to be a dimer, was also obtained. The preparation was repeated with larger quantities (1·5 gm. of CCXVIII) and gave up to a 30% yield of CCX.

Analysis of the compound melting at 143-5°C. :-

Experimental analysis: Br 23·7%

Theory for $C_{19}H_{11}OBr$ (CCX): Br 23·8%
253

Attempted Ring-Closure of 7-(ortho-Bromobenzylidene)-acenaphthene-8-one, CCX, (p. 166).

35 Mg. of dry 7-(ortho-bromobenzylidene)-acenaphthene-8-one (CCX), 1 ml. of quinoline and 0·3 gm. of potassium hydroxide were boiled under reflux for 70 min. The reaction mixture was then poured into 20 ml. of conc. HCl and yielded a brown precipitate from which no product was obtained either by extraction with benzene and crystallisation or by chromatography. The benzene extract had a yellow green fluorescence in ultra-violet light.

The reaction was repeated with 0·3 gm. of CCX, 2 ml. of quinoline and 0·8 gm. of KOH. The reactants were boiled under reflux with stirring for 90 min., a part being withdrawn and worked up after

30 min., but again no product was obtained.

Wolff-Kishner Reduction of 7-(ortho-Bromobenzylidene)-acenaphthene-8-one, CCX, (p. 167).[221,222,253]

1·2 Gm. of 7-(ortho-bromobenzylidene)-acenaphthene-8-one (CCX) and 0·5 ml. of hydrazine hydrate were dissolved in 15 ml. of ethylene glycol and 2 ml. of benzene and maintained at 100°C. for one hour. 0·5 Gm. of KOH were then added and the reactants were boiled under reflux for a further 45 min. The residues were acidified with HCl, extracted with ether and the extract washed, dried, boiled with charcoal and quickly steam distilled to yield 0·25 gm. of colourless needles which, when recrystallised from petrol, melted at 94-5°C. and and were proved by mixed melting-point determination to be composed of acenaphthene (VIII). Further crystallisation afforded 0·2 gm. of a colourless crystalline compound melting at 125-7°C. and a few milligrammes of a yellow compound of M.P. 323-5°C. The analysis of the compound melting at 125-7°C. suggested that it might be the expected 7-(ortho-bromobenzylidene)-acenaphthene (CCXXI).

Experimental analysis: Br 23·7%

Theory for $C_{19}H_{13}Br$ (CCXXI): Br 24·9%

Abstract of Thesis

The principal sections of this Thesis comprise syntheses of substituted fluoranthenes, namely: two syntheses of 10:13-diphenyl-11:12-benzfluoranthene, two syntheses of 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one (from one of which it could only be isolated as its known decomposition product 10:13-diphenyl-11:12-benzfluoranthene), and a synthesis of 10-phenylfluoranthene-12-borate (in an attempt to prepare 10-phenylfluoranthene).

One synthesis of 10:13-diphenyl-11:12-benzfluoranthene and 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one was from diphenylketene and 7-benzylideneacenaphthene-8-one, and one of the unstable intermediates from the reaction, 7-benzylidene-8-diphenylmethyleneacenaphthene, was isolated in solution and its ultra-violet spectrum recorded. The structure of the pentaphenyltetrahydrofluoranthenone, a previously unknown compound, was proved by its decomposition products, its properties, and the formative reaction, which was elucidated. An analogous series of reactions between 2-benzylidenehydrindene-3-one and diphenylketene afforded compounds believed to be 2-benzylidene-3-diphenylmethylenehydrindene and 1:2:2:4:4-pentaphenyl-1:2:3:4-tetrahydrofluorene-3-one.

The second synthesis of 10:13:diphenyl-11:12-benzfluoranthene was from sym-tetraphenylacetone and 7-benzylideneacenaphthene-8-one and involved the formation of 10:10:12:12:13-pentaphenyl-10:11:12:13-tetrahydrofluoranthene-11-one as an intermediate, but under conditions in which it was known to decompose to form 10:13-diphenyl-11:12-benzfluoranthene, and only the latter could, therefore, be isolated.

The formation of 10-phenylfluoranthene-12-borate was from 7-benzylideneacenaphthene-8-one and acetoacetic ester and involved the isolation and study of 10-phenyl-11-carbethoxy-10:11:12:13-tetrahydrofluoranthene-12-one and 10-phenyl-9:10:11:12-tetrahydrofluoranthene-12-one and a compound believed to be 10-phenyl-11-carbethoxy-9:10:11:12-tetrahydrofluoranthene-12-one.

Minor sections of this Thesis comprise studies of the α :β-unsaturated properties of 7-benzylideneacenaphthene-8-one by elucidation of the unorthodox reaction of the compound with PCl_5 and HCl, by studying the reducibility of the substance and its reactivity with other reagents which interact with α:β-unsaturated ketones (e.g. vinyl butyl ether, ketene, phenylketene, benzyl cyanide and cyanoacetic ester). 7-(ortho-Bromobenzylidene)-acenaphthene-8-one was also prepared and its ring-closure attempted.

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The ultra-violet spectra (q.v.) and the principal reactions set down in this Thesis are listed by the names of the compounds concerned, or the names provisionally allotted to them where identities are uncertain.

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